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The Atmospheric Effects of Stratospheric Aircraft: A Second Program Report

NASA

The Atmospheric Effects of Stratospheric Aircraft: A Second Program Report

Edited by
Richard S. Stolarski
Goddard Space Flight Center
Greenbelt, Maryland

Howard L. Wesoky
NASA Office of Space Science and Applications
Washington, D.C.

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The Atmospheric Effects of Stratospheric Aircraft: A Second Program Report

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Richard S. Stolarski
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, MD

Howard L. Wesoky
National Aeronautics and Space Administration
Office of Aeronautics
Washington, DC

Editors

Market and technology considerations (Lee, 1990) continue to provide an impetus for high-speed civil transport (HSCT) aircraft research. Because HSCTs would fly in the stratosphere, special emphasis must be placed on studies of the potential environmental effects of these aircraft. A recent scientific assessment, under the auspices of the United Nations Environment Program (WMO, 1991), has shown that considerable uncertainty still exists about the possible impact of aircraft on the atmosphere. The International Civil Aviation Organization has recently begun consideration of standards for aircraft cruise emissions of the oxides of nitrogen (NO_x) and other trace chemicals (ICAO, 1991).

The Atmospheric Effects of Stratospheric Aircraft (AESA) element of the High Speed Research Program (HSRP), which is funded by the NASA Office of Aeronautics and Space Technology, has been designed to develop the body of scientific knowledge necessary for evaluation of the impact of stratospheric aircraft on the atmosphere. In our first program report (Prather et al., 1992), the basic objectives and plans for AESA were described, and early research results presented. In this report, the status of the ongoing research will be described as reported by principal investigators at the second annual AESA program meeting in May 1992, or shortly thereafter. Subsequent reports will document the continuing progress of the program which is scheduled to continue through late 1995.

The research being carried out under AESA complements and draws heavily on the basic research and analysis programs of NASA. In particular, the laboratory and atmospheric observations elements of AESA are heavily dependent on the underlying base investigations of the Upper Atmosphere Research Program (UARP), which are funded by the Office of Space Science and Applications (OSSA). The AESA modeling element is closely tied to and dependent on the Atmospheric Chemistry Modeling and Analysis Program (ACMAP), also funded by OSSA. AESA support is used to emphasize those elements of UARP and ACMAP that are most relevant to the evaluation of the effects of stratospheric aircraft, and to focus the efforts of many of the researchers in those programs in the directions most beneficial to AESA.

A primary focus of AESA has been the impact of our rapidly increasing knowledge about heterogeneous chemical processes. A significant example of the importance of this research was provided by the Second Airborne Arctic Stratospheric Expedition (AASE-II). This mission was primarily sponsored by UARP, but supported by AESA. The AASE-II end of mission statement included the following:

"The importance of heterogeneous reactions on sulfate aerosols has been verified by these aircraft studies. Thus, the impact of additional NOx on ozone in the lower stratosphere is expected to be much smaller than previously predicted and now may be closer to that simulated with the most recent global assessment models that include heterogeneous sulfate-layer chemistry"

AASE-II provided data that demonstrated that heterogeneous reactions were significant in determining the chemical composition of the lower stratosphere at northern middle latitudes (see Chapter 6 for a more detailed discussion). These results are generally consistent with the idea that the reaction of N_2O_5 with H_2O occurs on the background aerosols at a rate near that measured in the laboratory. Models incorporating this reaction have been used to predict the ozone depletion that could be caused by proposed fleets of HSCT aircraft, and the results are summarized in Figure 1 (see Chapter 5 for a complete discussion). Although it is not known what level of ozone depletion may be acceptable, these predictions indicate that HSCT operation may result in smaller depletions of ozone than had been previously predicted by models incorporating only gas-phase chemistry (see e.g., CIAP, 1974, Prather et al., 1992).

The AASE-II measurements also raise a number of questions about the role of heterogeneous reactions on background aerosols versus volcanic aerosols, as well as on polar stratospheric clouds within and on the edge of the polar vortex. One new question that has been identified is whether the enhancement of ambient nitric acid and water vapor in heavily traveled corridors could lead to the formation of nitric acid trihydrate (NAT) clouds at middle latitudes. These clouds, if formed, would be equivalent to the polar stratospheric clouds. If such clouds form in corridors, then aircraft exhaust could possibly indirectly trigger ozone depletion through enhanced chlorine chemistry. Much more effort will be required to confirm and interpret the AASE-II measurements over the full operating range of possible future HSCT aircraft (i.e., geographic and seasonal effects may vary), but laboratory studies reported in Chapter 3 indicate the robustness of the conclusion that heterogeneous chemistry is playing an important role in the chemistry of the lower stratosphere.

To further pursue this matter, AESA is sponsoring another series of atmospheric measurements called the Stratospheric Photochemistry Aerosols and Dynamics Expedition (SPADE). Using an ER-2 aircraft as an instrument platform, SPADE will be flown from the NASA Ames Research Center at Moffett Field, CA in April and May of 1993. This campaign will utilize the basic instrument complement from AASE-II with the addition of 1) an ultraviolet/visible spectrometer developed by the Canadian Atmospheric Environment Service for flight aboard the Space Shuttle, 2) an OH/HO_2 instrument developed by Harvard University under AESA support, and 3) a CO_2 instrument developed by a second group at Harvard University under AESA support. SPADE will expand the excellent work of AASE-II by addressing the primary question:

• *What are the key chemical processes that potentially affect ozone levels in the part of the stratosphere most strongly influenced by stratospheric aviation?*

A secondary question to be addressed by SPADE is:

• *What will be the distribution of exhaust effluents in the stratosphere?*

The SPADE measurements will emphasize free radical chemistry over a full diurnal cycle at the northern midlatitudes, those most important to aviation.

Future plans for atmospheric observations include an ER-2 deployment in conjunction with the UARP-sponsored 1994 southern hemisphere expedition and the development and deployment of the Perseus high-altitude, remotely piloted vehicle. The plans for these expeditions will be described in more detail in the next Program report.

The prediction of the possible atmospheric impact of HSCT aircraft will greatly benefit from the knowledge gained from these aircraft observations. There are, however, other research topics being supported by AESA that are critical to obtaining the best possible assessment by the end of 1995. Continuing laboratory studies are probing the mechanisms responsible for many of the heterogeneous reactions that occur on stratospheric particles, as reported in Chapter 3. Our understanding of atmospheric dynamics is similarly improving as described in Chapter 4. Understanding how the atmosphere redistributes the aircraft exhaust is critical to knowing where the chemically perturbed air may be transported and how long it will remain in the stratosphere. This remains one of the more difficult aspects of the problem for the determination of error bounds.

The assessment of aircraft operational effects is also dependent on the ability to correctly simulate fleet operations. Chapter 2 discusses development of fleet fuel burn and emissions scenarios, which will be much more complete than those previously applied (Prather et al., 1992). Besides providing a detailed geographic distribution for fuel burn and exhaust emissions (i.e., 1

degree latitude by 1 degree longitude by 1 km altitude), the simulated fleets will include military as well as civil aircraft and also consider operations in the former Soviet bloc.

Table 1 indicates the principal investigators associated with AESA, and Chapter 7 provides brief summaries of many of their efforts. The large number of investigators for atmospheric observations and field experiments have primarily been involved with AASE-II or are currently involved with implementation of SPADE.

In closing, it should be noted that the next report in this series will effectively mark the mid-point for the AESA program. Plans include having the interim assessment reviewed by the National Research Council. In the next year it is also planned to add topics to the program (e.g., climatic impact and uncertainty analysis) that are appropriate to a mature assessment activity. An international assessment has been proposed as the culminating activity for AESA in 1995.

ACKNOWLEDGMENTS

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Table 1. AESA Principal Investigators

A. Theoretical Studies

2-D Global Chemical Models and Stratospheric Ozone Assessment

G. P. Brasseur/NCAR
A. R. Douglass/NASA Goddard
R. S. Harwood/University of Edinburgh, United Kingdom
I. S. A. Isaksen/University of Oslo, Norway
M. K. W. Ko/AER, Inc.
J. A. Pyle/University of Cambridge, United Kingdom
R. K. Seals/NASA Langley
R. L. Shia/AER, Inc.
D. J. Wuebbles/LLNL

3-D Chemical Transport Models and Longitudinal Asymmetry

G. P. Brasseur/NCAR
A. R. Douglass/NASA Goddard
R. A. Plumb/Massachusetts Institute of Technology
R. B. Rood/NASA Goddard
H. R. Schneider/AER, Inc.

Emissions, Plume Chemistry, and Other Modeling

A. J. Bilanin/Continuum Dynamics, Inc.
T. J. Dunkerton/NorthWest Research Associates, Inc.
V. U. Khattatov/Central Aerological Obs., Russia
C. E. Kolb/Aerodyne Research, Inc.
R. C. Miake-Lye/Aerodyne Research, Inc.
O. B. Toon/NASA Ames
K. K. Tung/University of Washington
R. P. Turco/University of California, Los Angeles
G. K. Yue/NASA Langley

Laboratory and Theoretical Studies of Chemical Mechanisms

W. H. Brune/Pennsylvania State University
K. L. Carleton/Physical Sciences, Inc.
D. R. Crosley/SRI International
R. R. Friedl/JPL
M.-T. Leu/JPL
M. J. Molina/Massachusetts Institute of Technology
K. R. Ryan/CSIRO, Australia
M. A. Tolbert/University of Colorado
D. R. Worsnop/Aerodyne Research, Inc.

Table 1. AESA Principal Investigators

B. Atmospheric Observations and Field Experiments

J. G. Anderson/ Harvard University
D. Baumgardner/NCAR
D. R. Blake/University of California, Irvine
K. A. Boering/Harvard University
W. H. Brune/Pennsylvania State University
K. R. Chan/NASA Ames
J. E. Dye/NCAR
J. W. Elkins/NOAA Environmental Research Lab
D. W. Fahey/NOAA Aeronomy Lab
G. V. Ferry/NASA Ames
P. Hamill/San Jose State University
S. Hipskind/NASA Ames
M. H. Hitchman/University of Wisconsin, Madison
K. Kelly/NOAA Aeronomy Lab
J. S. Langford/Aurora Flight Sciences Corp.
M. Loewenstein/NASA Ames
D. M. Murphy/NOAA Aeronomy Lab
P. A. Newman/NASA GSFC
S. J. Oltmans/NOAA Environmental Research Lab
L. Pfister/ NASA Ames
M. J. Prather/University of California, Irvine
M. H. Proffitt/NOAA Aeronomy Lab
R. F. Pueschel/NASA Ames
B. A. Ridley/NCAR
J. M. Rodriguez/AER, Inc.
F. S. Rowland/University of California, Irvine
G. W. Sachse/NASA Langley
P. J. Sheridan/NOAA Environmental Research Lab
A. F. Tuck/NOAA Aeronomy Lab
G. Visconti/Universita' degli Studi L'Aquila, Italy
C. R. Webster/JPL
P. D. Whitefield/University of Missouri, Rolla
J. C. Wilson/University of Denver
S. C. Wofsy/Harvard University
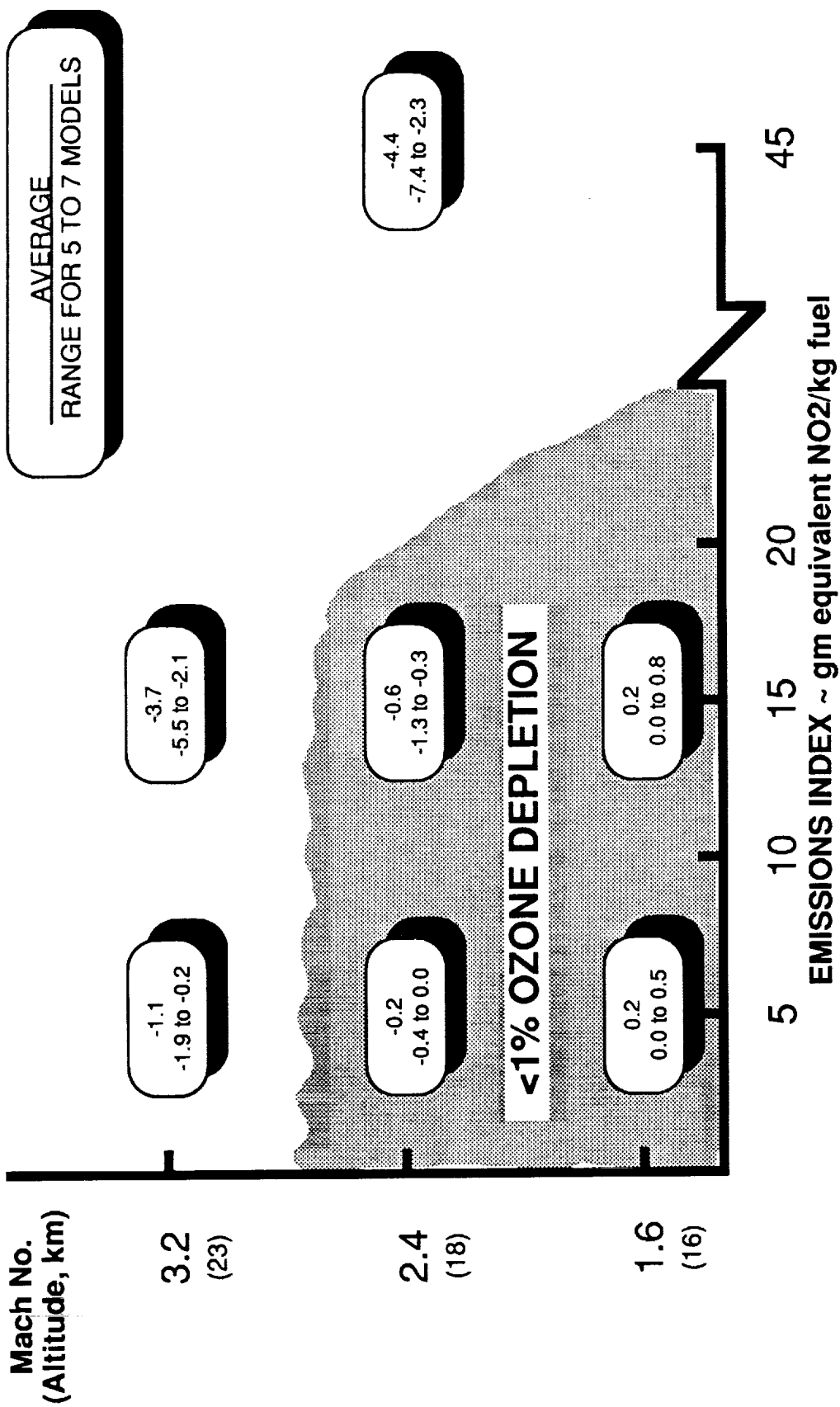
Figure 1. Calculated column ozone depletion at 40 to 50 degrees north latitude for high-speed civil transport operation in year 2015, assumptions include heterogeneous sulfate chemistry and 70 billion kg fuel/yr, approximately 600 M2.4 aircraft (see chapter 5 for complete discussion).

Chapter 2

Report of the Emissions Scenarios Committee: Preparations for the 1993 Assessment

Donald J. Wuebbles
Lawrence Livermore National Laboratory
Livermore, CA

Steven L. Baughcum and Stephen C. Henderson
Boeing Commercial Airplane Group
Seattle, WA

Richard Eckman and Donald Maiden
National Aeronautics and Space Administration
Langley Research Center
Hampton, VA

Munir Metwally and Alan Mortlock
McDonnell Douglas Corporation
Long Beach, CA

Felix Torres
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, OH

INTRODUCTION

An important step in the process of assessing the environmental effects of possible future High-Speed Civil Transports (HSCTs) is the definition of scenarios for the emissions from a fleet of such aircraft. When completed, these scenarios will be used in numerical models of the chemistry and physics of the global atmosphere, and the potential environmental effects, including concerns about changes in ozone and in climate, could be determined.

The Emissions Scenarios Committee was formed to provide a forum for meeting the combined needs of the atmospheric science community, the aircraft industry, NASA, and the federal government in undertaking the development of scenarios for such assessments. Current members of the Emissions Scenarios Committee are given in Table 1. At no other time in aviation history, including the days of the prior assessments of the supersonic transports in the 1970s, has there been an attempt to develop such a detailed database for aircraft emissions.

In a chapter for the first Atmospheric Effects of Stratospheric Aircraft/High-Speed Research Program (AESA/HSRP) report, Wuebbles et al. (1992) determined guidelines for the scenario development, such that the approaches taken in developing assessment scenarios must be detailed, justifiable, and fully documented (see Table 2). The methodology and algorithms used in the scenario development must also be flexible to meet the needs of the scientific, engineering, and policy-making communities.

The Emissions Scenarios Committee has met several times to discuss requirements and to develop priorities for the scenarios to be used in the 1993 interim assessment of the potential environmental effects of HSCTs. Much of the focus of the meetings has been on the algorithm development being completed by Boeing Commercial Airplane Group (referred to as Boeing or BCAG) and McDonnell Douglas Corporation (also referred to as Douglas or MDC) in preparing the scenarios for the 1993 interim assessment. Goals of the meetings were to establish the schedule, determine the scenarios to be analyzed, define and resolve problem areas in the scenario development process, and discuss possible opportunities for international participation and coordination. The current status in meeting the needs for the 1993 assessment is described in this chapter.

THE 1993 ASSESSMENT

The HSRP members expect the 1993 assessment to be largely completed at the future AESA/HSRP Annual Meeting. The National Research Council (NRC) of the National Academy of Sciences (NAS) will then review the status of HSCT research based on the outcome of the Annual Meeting. Once the various parts of the scenarios are completed, it will take about a month for the final scenarios to be made available to the modeling community, and then, in preparation for the assessment, a gridding principal investigator (at NASA Langley) will translate the scenarios onto an appropriate computer database. This leaves a relatively short time for the actual scenarios to be defined and the emissions algorithms to be developed.

It is premature to base scenarios on actual HSCT aircraft designs; such designs are only conceptual and do not fully exist. At the past meeting, eight scenarios were developed for the 1993 assessment. Those currently under development are summarized in Table 3. Scenarios of fuel burn and emissions (e.g., NO_x, CO, and hydrocarbons) are being developed for projected fleets of Year 2015 subsonic aircraft (both with and without an HSCT fleet); for HSCT fleets corresponding to Mach 1.6, 2.0, or 2.4; and for a Year 1990 subsonic fleet. The subsonic scenarios will evaluate the fuel burn and emissions for scheduled airliner (jet aircraft), scheduled cargo, scheduled turboprop, military, charter, and unscheduled air traffic. The Mach 1.6 and Mach 2.4 cases are representative of aircraft designs generally being considered in the U.S.; the

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Mach 2.0 cases correspond to designs more representative of those being considered in Europe. For each HSCT supersonic cruise altitude, scenarios are being developed for assumed NO_x emission indices of 5 and 15 grams of NO_x (as NO_2) per kilogram of fuel burned. Two different engine emissions indices are used to represent the range of uncertainties possible in the development of low NO_x combustors. Estimated emissions for a concurrent fleet of subsonic aircraft are to be included along with the HSCT emissions in the scenarios to be developed for approximately the year 2015. For comparison purposes, a scenario that assumes only subsonic aircraft in the 2015 fleet is to be developed. Emissions from the actual 1990 fleet are also to be evaluated and examined in model calculations. The evaluation of the existing (largely) subsonic fleet provides a relative basis for evaluating future environmental effects. It also provides a basis for projecting the 2015 emissions.

In order to generate these emissions scenarios, it is necessary to account for the aircraft performance, engine characteristics, and marketing data (flight frequencies, city-pairs, and routing). This scheme is summarized in Figure 1 which shows how the various components must come together to produce a geographical inventory of fuel burn and emissions.

The official HSCT scenarios for the 1993 assessment are limited to two NO_x emission indices and three Mach numbers because of the necessity to limit the number of scenarios. However, it may be useful that atmospheric models consider a wider range of sensitivity studies. Realistic emissions for an HSCT fleet with different emissions or flying at different altitudes cannot be directly scaled from the scenarios provided; however, sensitivity studies can largely capture the effects of such changes by using scaling.

REQUIREMENTS AND METHODOLOGY

The Wuebbles (1992) and Wuebbles et al. (1992) reports described the basic methodology to be used in the algorithm and scenario development. Table 3 shows the responsibility as divided between Boeing and McDonnell Douglas for development of the assessment scenarios; Table 4 shows the scenario methodology and algorithm development requirements developed for this assessment; Table 5 defines the criteria and responsibilities for developing the 1990 fleet emissions; and Table 6 similarly defines the criteria and responsibilities for the 2015 subsonic and HSCT scenarios. Although many of the criteria and requirements in these tables were discussed in the previous report, several important features are new. For example, because of proprietary concerns, the companies have difficulties in publishing their detailed evaluations of the flight characteristics for specific aircraft; this makes it difficult for them to fully document the 1990 fleet emissions. As a way around this, it was proposed that they develop generic aircraft types (an aircraft having the right kind of characteristics that can be used to represent similar aircraft from different companies). These generic aircraft would then be used to develop the 1990 fleet emissions and could be appropriately documented.

The necessity to include seasonality in the subsonic and HSCT emissions has also been considered. McDonnell Douglas analyzed commercial jet flights from 1976-1991 and found strong variations in the subsonic traffic with season (see Figure 2). This variation largely results from the strong influence of tourism. The HSCT traffic may be more dependent on business traffic and therefore less seasonal; nonetheless its seasonal variation could be important and will be evaluated. However, because of the limited time left for algorithm and scenario development, treatment of seasonal variations in the emissions will not be included in the scenarios to be evaluated for the 1993 assessment.

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ENGINE PERFORMANCE AND EMISSIONS

The total NO_x emissions produced by the various HSCT concepts depend on the operating conditions of the engine, the type of combustor used, and the profile of the mission flown. Currently, two types of advanced low-NO_x emission combustors are under consideration for use in HSCT propulsion systems, a lean-premixed-prevaporized (LPP) concept, which is being developed by General Electric (GE), and a rich-burn, quick-quench, lean-burn (RQL) concept that is being developed by Pratt & Whitney (P&W). Although the emissions characteristics have not been fully quantified, both appear to show promise of achieving the HSRP low-NO_x combustor emission index (EI) goal of 2 to 8 grams of NO_x per kilogram of fuel burned, based on laboratory flame tube results.

The HSRP NO_x goal is associated with the supersonic cruise portion of the mission profile. The operating characteristics of the low-NO_x combustor will change at other aircraft operating conditions. Typical mission operating conditions include:

- Takeoff
- Subsonic climb
- Subsonic cruise
- Supersonic climb
- Supersonic cruise
- Descent
- Approach.

The engine/combustor concepts selected for the three HSCT configurations at Mach 1.6, 2.0, and 2.4 in the emissions scenario development are as follows:

Mach 1.6   P&W Mixed-Flow Turbo Fan (MFTF) incorporating a general HSCT low-NO_x combustor

Mach 2.0   P&W Turbine Bypass Engine (TBE) incorporating a general HSCT low-NO_x combustor

Mach 2.4   P&W TBE incorporating a general HSCT low-NO_x combustor.

Note that the choice of engines in these scenarios in no way reflects on the engine development being done by GE or P&W.

A typical mission profile for HSCTs with a TBE engine design and general HSCT low-NO_x combustor having a nominal 5 EI NO_x at supersonic cruise conditions is shown in Figure 3a. The variation in EI during the complete mission profile is also indicated. In order to produce an HSCT emission scenario corresponding to an EI of 15, the EI=5 data will be scaled using scaling parameters recommended by the engine companies for each phase of the mission profile.

HSCT SCENARIOS

HSCT Passenger Demand

Forecast of Total Demand

Boeing and McDonnell Douglas annually publish world traffic forecasts and fleet outlooks for passenger and cargo traffic.* These reports contain the company forecasts of world air travel growth and the commercial jet fleet requirements that will satisfy passenger and cargo demands. These forecasts are based on sophisticated econometric models, which are used to predict the key economic variables that affect worldwide economic and traffic growth. Traffic projections take into consideration a variety of other forecasts that affect annual traffic growth rates such as:

- Changes in the cost of travel
- Changes in the income of the traveling population
- Specific changes in regional economies
- Demographic and political changes
- Proposed regulatory actions
- Airplane retirements.

Both the BCAG and MDC forecasts project traffic through the year 2010. For the purpose of developing the 2015 projected year emission scenarios, the regional demand forecasts were extended from 2010 to 2015.

The BCAG and MDC forecasting models project passenger demand for more than 20 world air traffic regions. For the purpose of producing a joint traffic projection through 2015, the regional growth rates of the two companies were averaged.

HSCT Traffic Demand

Because of the unique characteristics of supersonic operation, the airplane routes must be examined in terms of their suitability for supersonic flight. Only those suitable routes will be included in a supersonic network that will be used for the emission scenarios.

Markets that can be efficiently served by HSCT generally are those that are fairly long range and mostly over water. Domestic and intra-regional routes were excluded from the HSCT service network. Flight paths of each of the candidate city-pairs were constructed with the aim of minimizing overland (subsonic) flight, which greatly reduces HSCT time savings and efficiency. "Waypoint" routings to avoid overland flights can greatly improve the percentage of over-water flight for some routes with a small penalty in total miles flown. It was decided to exclude those city-pairs where excessive diversion might offset the time-saving benefits.

In order to sort out the routes that are HSCT compatible, BCAG and MDC have developed the following criteria for use in the selection process:

- Minimum distance 2000 nautical miles
- Overland segment is less than 50% of the flight distance
- Route diversion will not exceed 20% of the Great Circle distance.

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* Available from the Boeing Market Research Group and from Douglas Aircraft Company Market Development.

The resulting route network consists of approximately 250 city-pairs, the selection of which is currently being finalized by BCAG and MDC.

HSCT Frequencies and Fleet Requirements

The analysis by BCAG and MDC of HSCT traffic demand identifies the total passenger demand market accessible to a fleet of HSCTs. Since competition from subsonic airplanes for the same market will be intense, the HSCT is not expected to capture 100% of the market.

For purposes of developing HSCT emission scenarios for the year 2015, a fleet size of roughly 500 HSCTs has been assumed. This amount would probably represent an economically viable fleet. Since HSCT production is not projected to start before 2005, the total number of HSCTs by 2015 will also be limited by production rates as well as by the fraction of the market it can capture.

With the above assumption, the accessible passenger demand must be partitioned between the different available city-pairs. It is being determined whether this should be done by reducing the city-pair network (which would concentrate the HSCT on the routes best suited for its capabilities) or by scaling the accessible passenger demand while preserving all possible city-pairs (which would preserve the geographical distribution of emissions associated with a larger fleet).

Mach 1.6 HSCT Scenario Development

Douglas is developing a database for global atmospheric emissions from the projected Mach 1.6 HSCT using the supersonic network (market, routing, and fleet size) described above. The Mach 1.6 scenario draws upon Douglas configuration design studies, P&W/GE engine cycle data, and the aforementioned supersonic network to provide predictions for the amount and distribution of exhaust emissions.

Configuration Design Studies

Configuration design studies provided the Mach 1.6 airplane performance predictions, including the altitude and down-range distance of engine emissions. Douglas calculated the performance of the combined airframe and engine. Inlet conditions at the engine face were provided to P&W and GE. Given the inlet conditions, P&W and GE provided uninstalled engine thrust, fuel burn, and nozzle exhaust emission constituents. Douglas accounted for engine installation and operational effects on engine and airframe performance, which were integrated with the airframe design to create final HSCT performance predictions.

The configuration design shown in Figure 4 was developed from previous Mach 1.6 design optimization studies. It will be updated with the latest technology predictions, consistent with Douglas Mach 2.4 baseline studies. The design range will be 5000 nautical miles, and the HSCT will average 15% subsonic over land. A new Mach 1.6 engine cycle will be integrated into the design.

P&W Engine Cycle Data

The Mach 1.6 engine cycle data will be provided by P&W using the joint P&W/GE ground rules. P&W will provide an MFTF cycle employing low NO_x combustor technology. The Mach 1.6 ground rules and combustor technology will be consistent with Mach 2.0 and 2.4 technology.

Calculation of Exhaust Emissions

Once the configuration design and marketing/economic studies are completed, the final HSCT design will be flown in a similar manner throughout the supersonic network, and exhaust emission

constituents will be distributed across the globe. Performance data from the configuration design studies will be used to develop a parametric formula for calculating fuel burn as a function of range, load factor, and percent over land. An input file will describe the altitude and downrange distribution of fuel burn as a function of the distance over land or water, and whether a climb or descent is needed at the beginning or end of the distance (to allow for waypoint routing). The formula and file are used with the supersonic network to determine the fuel burn distribution from each HSCT route flown each year. These values are stored as a file of fuel burned versus downrange distance and altitude. This fuel burn information is combined with a second input file that describes EI as a function of altitude. As the emissions for each constituent are calculated for each altitude along the route, they are also distributed in latitude and longitude across the global atmosphere.

Mach 2.0 HSCT Scenario Development

Boeing will determine the Mach 2.0 HSCT scenario based on an analysis of performance and fuel burn characteristics using the same engineering ground rules as were used to design the Mach 2.4 HSCT (see detailed discussion below). Engine-specific fuel consumption and emissions will be provided by Pratt & Whitney for the chosen baseline engine. HSCT fuel burn characteristics will be based on calculated installed engine performance as a function of mission range, fuel requirements, weight, etc. The city-pairs and routing will be the same as were used in the Mach 2.4.

Mach 2.4 HSCT Scenario Development

The Mach 2.4 HSCT scenario will be based on the Boeing design for a Mach 2.4 HSCT and the engine selected as a baseline for evaluation of the aircraft performance. Engine-specific fuel consumption, weight, and emission characteristics were provided by Pratt & Whitney (see Figure 4b). Boeing's HSCT propulsion group "installs" the engine on the HSCT with an inlet and exit nozzle, including the weight and performance penalties associated with other design requirements (such as low takeoff noise). The propulsion group then takes the physical dimensions and weights of the combined inlet-engine-nozzle system and places the accessories (heat exchangers, starters, gear-boxes, tubes, connectors, etc.) that will be required for operation. They also include installation effects of the inlet (in terms of internal inlet performance; airflow capability; and inlet spillage, bypass, and bleed drag) and the nozzle (in terms of the internal nozzle performance, thrust coefficient, and external performance) to modify uninstalled engine performance. Thrust and associated thrust-specific fuel consumption (TSFC) are adjusted for the installed engine performance system. These factors directly affect the amount of engine emissions. Engine emissions are a function of the engine power setting and are thus calculated directly from the required engine power at a given leg of a mission.

Based on the aerodynamic performance of the aircraft and the performance of the installed engine, the fuel burn and emissions for individual missions are calculated. For each leg of a mission (e.g., takeoff, climb, cruise, descent), the power setting (thrust required) can be calculated and used to determine the fuel consumption rate and the emissions (NO_x, CO, and hydrocarbons). The calculation process is repeated for parametric missions cases: various takeoff weights (corresponding to different amounts of fuel for different range missions), different passenger loading factors, and different cruise speeds (Mach 2.4 and Mach 0.9).

For the current scenarios, it is assumed that supersonic overland flight will not be allowed, and thus the HSCT must either descend to fly subsonically over land or use waypoint routing to avoid land masses. Mission profiles of altitude, fuel burn, and emissions explicitly account for these waypoints. Based on these mission profiles, the fuel burn and emissions are then calculated onto a 1° x 1° x 1 km grid assuming great circle routing between waypoints. As an example, a schematic of a possible mission involving subsonic flight over land in mid-mission is shown in Figure 3b.

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EVALUATING 1990 EMISSIONS

Scheduled Air Traffic

Data on the city-pairs, flight frequency, and aircraft type of 1990 scheduled air traffic (airliner, cargo, and turboprop) are available from the Official Airline Guide (OAG). For the scenarios currently under development, great circle routing will be assumed for all flights. Fuel burn and emissions near airports will be accounted for using typical data for each aircraft type. Mission profiles will be assumed to be a cruise climb. It is anticipated that in later studies, the error (probably negligible) associated with this assumption will be estimated relative to the more realistic step climbs used to satisfy air traffic control. Based on the distance to be traveled, the aircraft's flight altitude, speed, and fuel usage will be computed. A fuel burn rate at discrete locations in each flight segment will then be calculated using fuel burn and emission characteristics of actual aircraft/engine combinations now in service and available in Boeing's engineering database. Approximately 50 aircraft/engine combinations will be used in these analyses. Other aircraft/engine combinations will be approximated by one of these.

Emission characteristics (NO_x, CO, and hydrocarbons) are available for each engine as part of the International Civil Aviation Organization (ICAO) certification process. The data are limited to a few points at discrete power settings at sea level. For these mission analyses, the available emission data are parameterized as a function of fuel burn rate (thrust setting). Although not as accurate as using emission index versus combustor inlet temperature (as recommended by the engine manufacturers) this approach does provide a means of calculating emissions for each mission without running engine-specific performance-cycle computer code. The latter alternative would be prohibitively expensive for a global emission scenario in terms of both computer requirements and manpower. The corrections for altitude are based on information provided by the engine manufacturers.

The global atmospheric emissions computer code (GAEC) calculates the gridded emission scenarios by opening a file of all routes flown by a particular airplane type. Great circle distances are then calculated and stored for each route. Using the total distance to be flown, airplane performance tables are accessed to determine fuel flow rate, airplane gross weight, time and altitude at route/cell boundary intercept locations. With this information, the total fuel and fuel flow rate are then stored in the appropriate geographical cell (latitude, longitude, altitude) that the flight has crossed. Significant fuel flow rate differences within a cell, which indicate a change in flight condition, will be accounted for. The fuel flow rate, altitude, and aircraft type are then used to look up emissions from engine emission tables. The emissions and fuel usage for each route are then multiplied by the daily frequency of flights by that aircraft on that route.

A similar process will be used for both scheduled cargo and turboprop traffic. For turboprop aircraft, a much simpler engineering description will be used wherein the aircraft are categorized into two categories according to passenger load and the approximate fuel burn and emission characteristics estimated for each. The turboprop fleet will then be "flown" in GAEC as described above for the airliner traffic.

The above description applies to the generation of an actual 1990 airliner fleet based on an extensive engineering database available at Boeing. This gridded scenario will be published and publicly available. In order to document these scenarios, a "generic" airplane performance database will be generated which can be released.

The generic combinations will be based on the same eight classes of aircraft used in Boeing's Current Market Outlook (Table 7), thereby providing a standard basis upon which to forecast the year 2015 fleet. Within each class of airplane a weighted average of departures and cruise fuel burn per seat-mile will be used to obtain a generic airplane model within the class. Within each

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class, the actual airplane performance and engine emission tables will be weighted together at a suitable number of discrete integration points. For generic emissions, similar averaging parameters will be used along with the cruise emissions index of each emission type. Using GAEC, a global, gridded emission scenario will then be generated using the "generic" 1990 aircraft types.

The gridded 1990 actual and "generic" scenarios will be compared to establish some estimate of the errors associated with the "generic" approach. Because there are regional differences in aircraft in operation even within a given size class, some differences between the two scenarios are expected. Calculated scenarios will be provided to NASA as electronic data files.

Military, Charter, and Nonscheduled Eastern Europe and Chinese Air Traffic

The development of the emission database for military, charter, and nonscheduled (non-OAG) Eastern Europe and Chinese air traffic are discussed in this section.

Military Air Traffic

I. Objective

The engineering database of worldwide military air traffic data for 1990 and a complementary database of associated engine emission indices are being developed to be used in AESA/HSRP studies.

The military air traffic data are composed of representative aircraft types, locations, flight routes, flight frequencies, and fuel burn profiles. For this study, the emission constituents of interest are carbon monoxide, oxides of nitrogen, and total hydrocarbons. In a separate task, combination via computer processing of the military air traffic data and the emissions data will result in the generation of 1990 fuel burn and emissions grids with a resolution of 1° (latitude) x 1° (longitude) x 1 kilometer (altitude).

II. Methodology

A. Inventory of Military Aircraft

A long list of military sources, U.S. and international, was used to account for the worldwide fixed-wing fleet (see references in Appendix). As a result, consistent and complete military equipment data organized primarily by military alliances and geographic regions are provided for 147 countries.

Within each country, the military organization is given according to service followed by an equipment list. In general, the aircraft are grouped by the mission they perform. For each country, the data include aircraft owned by foreign nations but based in its territory. Foreign deployment assignments are also listed for the U.S. Figure 5 shows 140 countries owning about 67,000 aircraft. Notably, three countries, the former USSR, the U.S., and China, account for 49% of the entire fleet.

B. Aircraft and Mission Profiles

The aircraft in the 1990 worldwide inventory represent many unique aircraft designs and derivatives numbering in the hundreds. The variety of aircraft in the inventory range from high-technology, front-line fighter aircraft with state-of-the-art power plants to 1940s vintage transports equipped with radial engines. Many of these aircraft also have commercial applications; for example, the U.S. Air Force C-9A Nightingale, an aeromedical airlift transport, is a derivative of the DC-9 Series 30 commercial airliner. The approach undertaken in this study is to use generic

aircraft to represent each aircraft type in the 1990 inventory; specifically, for each combination of military mission and region/alliance, a single aircraft is used to represent all aircraft in that combination.

Specific missions considered include fighter/ground attack, counterinsurgency, bomber, transport, tanker, trainer, maritime patrol, electronic warfare, and reconnaissance. Region and/or alliance categories are (tentatively): U.S., NATO (excluding U.S.) and Western Europe, former USSR, Eastern Europe, China, Caribbean and Latin America, Middle East and North Africa, Sub-Saharan Africa, and other Asian and Australasian countries.

Initially, the data are reduced by mapping specific aircraft into a set of representative aircraft for which performance data are available. This process is outlined in Figure 6. The mapping is based on a subjective assessment of aircraft characteristics such as engine quantity, power (thrust or horsepower), and type (turbofan, turbojet, propeller, etc.); maximum gross weight; wing configuration; performance; and vintage. *Jane's All the World's Aircraft* (Jane's Information Group Limited, Surrey, UK, 1942-1990) and "Specifications" in *Aviation Week and Space Technology* (McGraw-Hill, Inc., New York, 1991) are the sources for the aircraft characteristics data. The mapping results in an assignment of a representative aircraft and a fuel burn multiplier to each aircraft in the inventory. The fuel burn multiplier attempts to fine tune the mapping by scaling the fuel consumption of the representative aircraft to better reflect its expected fuel consumption.

Development of generic aircraft follows the mapping process and considers the distribution of aircraft by region and mission. Each region is sampled such that the total quantity of aircraft possessed by the countries constituting the sample account for at least 50% of the total aircraft in the region. Then, for each mission, the distribution of (mapped) representative aircraft and associated fuel burn multipliers is subjectively analyzed. The generic aircraft reflects a predominant representative aircraft and fuel burn multiplier or, where feasible and where no single aircraft dominates in quantity, a weighted blend of the most numerous representative aircraft.

Representative aircraft missions used in the study are based on standard mission information contained either in Standard Aircraft Characteristics (a U.S. Air Force series of publications), MIL-C-005011B (Standard Aircraft Characteristics and Performance, Piloted Aircraft, 1977), or the aircraft's performance manual. All aircraft fly radius missions, i.e., they fly a fixed distance along a great circle route and, depending on the mission, either land and return to the origin or return to the origin without landing. Mission segment elapsed time and distances, altitudes, and cumulative fuel burns are calculated using manufacturers' performance data. Figure 7 depicts a typical mission profile for the A-4m aircraft.

C. Engine Emission Indices

The constituents contained in aircraft exhaust emissions have been examined in numerous previous studies. Therefore, a substantial database of emission indices exists in the literature. This effort relies primarily on the work of Pace (1977), Sears (1978), and ICAO (1989) for emission indices data:

In this study, data on three constituents--hydrocarbons, carbon monoxide, and oxides of nitrogen--were collected for the engines associated with the representative aircraft discussed above. For each engine and constituent there is a set of relevant EIs. An EI measures mass of constituent emitted per mass of fuel consumed. It characteristically varies directly as a function of throttle setting for oxides of nitrogen and inversely as a function of throttle setting for both hydrocarbons and carbon monoxide. In essence, EIs measure combustor cleanliness for a given engine cycle.

As an illustration, a set of indices is shown below for the Allison T-56 turboprop engine.

Power Setting	Fuel Rate (klb/hr)	Emission Indices (lb/klb fuel)		
		CO	NO$_x$	Total HC
Idle	0.548	31.9	3.8	21.0
Approach	1.053	3.5	7.4	0.5
Intermediate	1.908	2.4	9.2	0.5
Military	2.079	2.1	9.3	0.4

Much of the previous work on emission factors has focused on concentrations of emissions in proximity to airports. Therefore, a significant portion of the available data only addresses engine power settings common to the landing-takeoff cycle: taxi/idle, takeoff, climb, and approach. Interpolation is used in those cases where data are not available for an appropriate "cruise" power setting. Also, altitude is assumed to have no effect on the magnitude of the constituents.

D. Aircraft Basing

Once again, the size and scope of the task calls for creative solutions. The problem of basing a global fleet is a primary driver in the task's level of detail. The amount of time it takes to base the aircraft in any given country is proportional to both the number of aircraft and the number of bases in that country. A trade study on aircraft basing shows that it is not practical to base every military aircraft in the world in its exact location. Additionally, data required for such a task are not readily available. Therefore, the concept of centrally basing aircraft has been adopted.

Centrally located basing involves selecting an airfield at or near the geographic center of a country and flying all of the aircraft in the country, as represented by the generic aircraft, from that geographic point. This solution was deemed adequate for the majority of countries having fixed-wing military aircraft. The base for a country is chosen using the *National Geographic Atlas of the World*, 5th Edition (1981) and selecting an airfield near the country's geographic center. The airfield coordinates are taken from the Military System Analysis Airfield Report (Vermeeren, July 1991). If the airfield is not listed in the report, the Atlas serves as the second source. Because of their size, some countries, e.g., Canada, might require additional bases to more correctly describe their basing status. Three countries in particular, the former USSR, the U.S., and China, are not based centrally because of fleet size and geographic considerations.

The former USSR maintains the world's largest fleet of military aircraft, i.e., it accounts for 21% of the entire global fleet. The nation is divided into Theaters of Military Operations, a Central Reserve Theater, and a Northern Front Theater, all further subdivided into Military Districts (MDs). These aircraft will therefore be based at or near the center of that district. Within a theater, the forces not assigned to a particular MD will be evenly distributed between the districts in that theater. The strategic forces, including long-range bombers and reconnaissance aircraft, are based in this manner.

The U.S. fleet of military aircraft is the second largest in the world, accounting for 18% of the total. The U.S. is divided into five regions as shown in Figure 8. Central basing of each region depends on the mix of operational missions of the region's bases. For example, if in the U.S. fleet, all fighters and other tactical aircraft are represented by 5000 generic aircraft, type F1, and region III has 10% of U.S. TAC bases, then 500 type-F1 aircraft will be based at the centroid of region III. According to basing data from MILAV News (Aviation Advisory Services Ltd., UK), naval aircraft are based at appropriate naval bases within four of the five regions. The Marine Corps aircraft are included in the naval force total and are distributed accordingly.

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The Chinese military aircraft fleet represents roughly 10% of the world's air forces. The aircraft are mostly variants of dated Soviet designs. Available data allow for a basing scheme similar to that used for the former USSR. Circa 1990, China was separated into seven Military Regions and then into Military Districts. Air Force aircraft are based in each region according to need. Districts bordering the former USSR and the coasts near Taiwan require a higher concentration of aircraft than others due to political tension. Naval aircraft are based at naval headquarters within the Guangzhou, Nanjing, and Jinan military regions.

For each generic aircraft type, three directions of flight are randomly generated. Where practical, they are routed over indigenous territory and not over water. However, this routing choice depends on the mission range of the aircraft, the geographic location of the country, and the country's shape. Only the naval aircraft of the U.S. and China are directed over water.

III. 1990 Global Fuel Burn Estimate

To estimate the contribution of military aircraft to global fuel burn, it is first necessary to postulate a flight frequency, or utilization rate, for each country's inventory of military aircraft. Doing so involves several assumptions. The global utilization rates (in terms of flying hours per year or fh/yr) are derived using U.S. Air Force data.

For any given country, some of the military aircraft will not be operational at some point during the year. In the U.S., failure to meet maintenance requirements and the lack of backup or spare aircraft are two reasons why an aircraft may be deemed non-operational. Funds to support flying hours (and, indirectly, utilization rate) for U.S. Air Force aircraft are based on a unit's Primary Aircraft Authorization (PAA). According to Air Force Regulation 173-13, "U.S. Air Force Cost and Planning Factors" (Headquarters U.S. Air Force, Washington, D.C., 1989), PAA represents the number of aircraft "... authorized to a unit for performance of its operational mission." Typically, PAA will be some fraction of the total aircraft possessed by a unit. The remaining aircraft allow for "... scheduled and unscheduled maintenance, modifications, and inspections and repair without reduction of aircraft available for the operational mission." Examining the ratio of operational aircraft to total aircraft for the U.S. Air Force F-15 and F-16 fleet shows that roughly 75% of this fighter fleet is available to meet current flying requirements. This same percentage should apply to aircraft for which the primary role is pilot training. Higher cost aircraft such as the bombers, large transports, and electronic surveillance and/or reconnaissance platforms, tend to have a higher ratio of operational aircraft to total aircraft; for the purpose of this study, 90% has been assumed.

U.S. utilization rates per PAA, based on a sample of representative aircraft programmed flying hours (fh) for 1989 from Air Force Regulation 173-13, are tabulated by mission below:

Mission	fh/yr/PAA
Fighter/Attack	332
Transport	676
Bomber	374
Trainer	546
Tanker/Reconnaissance/Other	335

Other countries do not necessarily use their military aircraft at the same rate as the U.S., and no data have been located that would allow a comparison. However, experts in the area of military operations have been consulted and agree that the approximations below are not unreasonable for the 1989-1990 time frame:

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Region/Country	% of U.S. fh/yr/PAA
NATO	100
Soviet Union/Warsaw Pact	75
China	50
Other	50

Combining the above scaled utilization rates with the ratio of operational aircraft to total aircraft yields an approximation of the annual flying hours by mission for each aircraft within each country's total fleet (the results have been rounded to the nearest 25).

Mission	U.S./NATO	Former USSR/ Eastern Europe	China/Other
Fighter/Attack	250	175	125
Transport	600	450	300
Bomber	325	250	175
Trainer	400	300	200
Tanker/Recce/Other	300	225	150

Single-sortie trip time comes from the flight planning process discussed in Section III. Therefore, estimates of the annual frequency of flights (trips/year) per aircraft can be derived using the above utilization rates. Flight frequencies, mission profiles, and aircraft inventories can be combined to gauge fuel burn quantities.

Charter Air Traffic

I. Objective

MDC is assembling an origin-destination matrix representing a normalized global distribution of the commercial nonscheduled air traffic. The origin-destination pairs are to reflect the most frequent actual combinations used by the nonscheduled operators. They will then construct a model global network to simulate nonscheduled services by appropriately selected generic aircraft.

II. The Data Base

Nonscheduled traffic data in the literature are usually presented in the aggregate form, which obscures the actual origin-destination information. There is no convenient publication that identifies nonscheduled origin-destination traffic, like the OAG for scheduled traffic. Consequently, a search was initiated for related data sources that could be used to synthesize the desired origin-destination distribution. Since better than 90% of the nonscheduled traffic originates in only two global regions--Europe and North America--a literature search was focused on these two regions and the referenced data sources were identified.

The ICAO (1990) reports annual statistics of nonscheduled traffic originating in the domicile country of the reporting airlines. The data, which cover both passenger and system performance measures as reported by 128 airlines from 68 countries, formed the basis for disaggregating the total regional data into the respective constituent countries.

The ITA (1990) report discusses the potential development of the European Charter operations under the umbrella of the emerging common market. It presented tables of passenger origin-destination distribution from the three major European nonscheduled traffic generators (Britain, Germany, and France) to 30 countries around the world. This report formed the basic European matrix of origin-destination distribution.

The Statistics Canada (1989) report presents detailed nonscheduled traffic statistics from all Canadian airports to all destinations identified by global region and specific destination within the region. The top four Canadian airport origins and the top three destination regions formed the Canadian portion of the North American matrix of 4 by 23 origin-destinations.

The U.S. International Air Travel Statistics (1990) report is similar in nature to the Canadian report. The top 15 U.S. airports handled 93% of the nonscheduled U.S. traffic. This combination of origin-destination formed the U.S. matrix of the North American region.

III. The Nonscheduled Traffic Network Model

The global origin destination matrix results from merging the three regional passenger distribution matrices and referencing each one to the total annual passenger traffic allocated to it from ICAO (1990). This normalizing procedure adds the flexibility of adjusting the total traffic level represented. For the purpose of network model building, each origin and destination was assigned an appropriate OAG airport code, geographical coordinates and computed airport-pair distance. The total annual nonscheduled departure data from ICAO (1990) were assigned to each origin-destination pair in conformance with the synthesized passenger distribution. Passenger load factor was assigned on a regional basis based on the reported performance in ICAO (1990). The resulting seat/trip grouped in capacity levels of 134, 172, and 334 seats. Each airport-pair is assigned an aircraft from a fleet of six generic aircraft based on capacity and range. Each generic configuration has its own Block Time and Fuel Burned Characteristics.

MDC total World Traffic Forecast, Figure 9, identifies five domicile origin regions of non-schedule traffic: Europe, Far East, Latin America, Middle East and Africa, and North America. Notably, the European and North American regions originate most of the traffic, with negligible contributions by the others. As a rule-of-thumb the magnitude of the nonscheduled traffic is about 10% of the total global scheduled traffic.

The maximum possible origin-destination combinations of 652 end up to be only 298 active combinations. Figure 10 shows the resulting global distribution by range of these combinations. The top 100 combinations were selected by Revenue Passenger Kilometers (RPK); these combinations appear to be a fair representation of the range distribution and were selected as the basis for the nonscheduled traffic network model. The 1990 traffic level from the MDC traffic forecast was imposed on the 100 airport-pair network, and the resulting generic fleet size of 540 units is in excellent agreement with the ITA report data.

Eastern Europe and China Air Traffic

Over the years MDC has developed an extensive database about world airlines, including those of the Eastern European countries and China that includes both scheduled and nonscheduled traffic for over 150 carriers. Efforts were made to identify nonscheduled air traffic for Eastern Europe and China as well as the scheduled domestic traffic that had not been reported in the OAG.

Nonscheduled Eastern Europe and China traffic was extracted from the following airlines' data bases:

> Adria
> Aeroflot
> Air China
> Balkan - Bulgarian Airlines
> China Airlines
> Czechoslovak Airlines
> Lithuanian Airlines
> Lot - Polish Airlines
> Malev - Hungarian Airlines
> Tarom - Romanian Airlines
> Yugoslav Airlines

The aggregate Annual Seat Mile (ASM) for the nonscheduled traffic of the above airlines in 1990 equaled 9.93 billion ASM, which, when compared to world passenger traffic, represents less than one percent. On the other hand, the scheduled traffic that was not reported in the OAG is of greater magnitude. For example, Aeroflot's 1990 scheduled traffic that was included by IATA in the World Air Transport Statistics Report No. 35 amounts to 172,798,781,000 ASM. Although all the traffic was reported as scheduled traffic, only 26% was reported in the OAG. The balance of Aeroflot's scheduled traffic equals 128 billion ASM. China's 1990 traffic as reported to IATA was approximately 30 billion ASM, of which one-third was captured by Air China and two-thirds by China Airlines. Traffic reported for China in the OAG totals 18 billion ASM, leaving 12 billion unaccounted for.

For the 1990 Eastern Europe and China emissions scenario, the air traffic database includes the following:

Nonscheduled traffic	9.93 B
Aeroflot scheduled traffic	127.94 B
China scheduled traffic	11.86 B
Total 1990 ASM	149.73 B

This traffic was distributed over a representative domestic network of 88 routes in these regions.

ESTIMATING 2015 SUBSONIC EMISSIONS

Scheduled Air Traffic

The Boeing marketing department will forecast the year 2015 demand as an extrapolation of the annual Boeing market forecast, which is publicly available. The process has been described earlier. This projection will be based on the year 2015 generic aircraft types, as suggested by the projected aircraft for 1992-2010 in Table 8. Flight frequencies and equipment types between city-pairs will be projected.

Due to the difficulty in predicting new technology and new regulations, the year 2015 projections will be simple scalars of the existing performance and emission characteristics. The intent will be to provide a methodology upon which to base future projections.

Unscheduled Air Traffic

MDC's military market analysis group will forecast the military fleet requirements for the year 2015. The military air traffic data will include aircraft types, locations, flight routes, flight schedules, and fuel burn profiles. The projection will be based on the generic military aircraft types that are projected for the year 2015. See the Appendix for references.

Charter traffic for the year 2015 will be based on the 1990 traffic level. The potential HSCT participation in nonscheduled charter traffic is based on the criterion that only routes with ranges greater than 2000 nautical miles are candidates for the service. The results show that HSCT will capture about one-third of the predicted charter traffic. The remaining traffic will be serviced by the generic subsonic fleet.

Eastern Europe and China air traffic for 2015 are being based on the 1990 traffic levels.

PRIORITIES/SCENARIO DEVELOPMENT

Based on the prior discussion, it is possible to list the priorities in the scenario development for the 1993 assessment. Such a list is given in Table 8. The priority of the scenario is to have a realistic database from which to evaluate the possible impact of a future fleet of HSCTs. Thus, the first priority is to complete the 2015 HSCT scenario. However, as mentioned earlier, the 1990 scenario provides a relative basis for evaluating future scenarios and is needed as well.

EMISSIONS DATABASE FOR ASSESSMENT MODELS

Electronic files of the emissions scenarios on the 1° x 1° x 1 km grid will be delivered to the Upper Atmosphere Data Pilot (UADP) computer system located at the NASA Langley Research Center. Due to the varying horizontal and vertical resolutions employed by models, the scenarios will be regridded at Langley into formats suitable for each of the participating modeling groups. Although two-dimensional models (such as those at LLNL, AER, NASA GSFC, and NCAR) will be the primary ones used in the assessment, some calculations with global three-dimensional models are also planned.

The UADP group will obtain grid requirements and develop techniques for the interpolation of emission scenario data in terms of latitude and height. Because the database will initially be used extensively in two-dimensional modeling assessments, the data must also be averaged in longitude. The subsonic and supersonic emissions, which are delivered separately to the UADP database, will be added together prior to the regridding process; they can also be made available separately.

The regridded scenarios will be made available to the modelers. The UADP database will also serve as the storage site for model results. Graphical visualization of the stored model results will be performed at Langley in collaboration with each modeling group in preparation for the 1993 HSRP annual meeting.

At present, the UADP system consists of two Sun workstations, a SparcStation 1+ and a SparcStation 2, each with 32 MB of memory and a total of 5 GB of disk storage. An erasable-optical disk system and magnetic tape backup units are also available. These systems will employ Oracle software as the primary interface between the end-users and the on-line databases. Electronic access is available over the internet and DECnet networks.

The UADP system was first placed in operation in 1986 to maintain satellite (e.g., LIMS, SAMS, SBUV) and selected balloon measurements and to provide electronic network access,

display software, and data manipulation capabilities to the research community. Database activities were expanded to support both the 1987 and 1988 stratospheric model intercomparison workshops and the AESA/HSRP model and measurements comparison held February 1992. The UADP program also provided the final graphical results for intercomparison workshop reports and for the 1991 UNEP assessment report. Other UADP activities include the formulation of a trace gas climatology to serve as a common model and reference for data processing in support of the Upper Atmosphere Research Satellite (UARS).

FUTURE CONSIDERATIONS

Beyond the current preparations for the 1993 assessment, there are a number of activities of interest that will require further scenario analyses in order to evaluate the potential effects of HSCTs. These activities will contribute to improving the emissions modeling capability for the planned 1995 international assessment and to providing emissions data for interim sensitivity studies. At this point, the suggested continuing studies include:

- Evaluate HSCT seasonal variability and its resulting impact

- Perform detailed analyses of routing variations resulting from sensitivity to atmospheric conditions or other operational concerns (e.g., to avoid the polar vortex)

- Calculate the seasonal variability in the subsonic fleet scenarios for each month using the OAG data (this is straightforward but time consuming and data intensive)

- Update the existing HSCT scenarios based on results from the AESA/HSRP assessment, e.g., altitude modifications in certain areas

- Calculate how the geographical distribution would change for a longer range HSCT

- Conduct a fleet growth study (How would geographical distribution change as the fleet grew larger?)

- Calculate a low sonic-boom configuration HSCT scenario (lower altitude overland or possible supersonic corridors overland).

ACKNOWLEDGMENTS

Table 1. Members of the Emissions Scenarios Committee

Donald J. Wuebbles, chair	LLNL
Donald L. Maiden, vice chair	NASA, Langley
Steven L. Baughcum	Boeing
Willard J. Dodds	GE Aircraft Engines
Samuel M. Dollyhigh	NASA / Langley
Richard Eckman	NASA / Langley
Thomas L. Galloway	NASA / Ames
John H. Gerstle	Boeing
William L. Grose	NASA / Langley
Malcolm K. W. Ko	AER, Inc.
Nicholas P. Krull	Federal Aviation Administration
Richard L. Kurkowski	NASA / Ames
Joel Levy	Environmental Protection Agency
Robert Lohmann	Pratt and Whitney
Munir Metwally	Douglas Aircraft Company
Rick Miake-Lye	Aerodyne Research, Inc.
Alan K. Mortlock	Douglas Aircraft Company
Robert Oliver	Institute for Defense Analyses
Michael J. Prather	University of Calif., Irvine
Richard Stolarski	NASA / Goddard
Felix J. Torres	NASA / Lewis
Howard L. Wesoky	NASA Headquarters
Allen L. Whitehead, Jr.	NASA / Langley
Kathy A. Wolfe, exec. secy.	ARC Professional Services Group

Table 2. Requirements for the Assessment Scenario Database

Well documented

Publicly available (published)

Actively scrutinized and approaches reevaluated

Flexible (to meet needs of the community)

Uses separable programs and algorithms

Open ended

Scenarios continuous in space and time

Table 3. Scenarios for which Detailed Databases Will Be Developed for the 1993 Assessment

1) 1990 Fleet	Scheduled (OAG) airline	Boeing
	Scheduled (OAG) cargo	Boeing
	Scheduled (OAG) turboprop	Boeing
	Charter	Douglas
	Military	Douglas
	Other (internal Russia, etc.)	Douglas
2) 2015 Subsonic	Scheduled (OAG) airline	Boeing
	Scheduled (OAG) cargo	Boeing
	Scheduled (OAG) turboprop	Boeing
	Charter	Douglas
	Military	Douglas
	Other (internal Russia, etc.)	Douglas
3) 2015 Subsonic* + Mach 1.6 HSCT (EI = 5)		Douglas
4) 2015 Subsonic* + Mach 1.6 HSCT (EI = 15)		Douglas
5) 2015 Subsonic* + Mach 2.0 HSCT (EI = 5)		Boeing
6) 2015 Subsonic* + Mach 2.0 HSCT (EI = 15)		Boeing
7) 2015 Subsonic* + Mach 2.4 HSCT (EI = 5)		Boeing
8) 2015 Subsonic* + Mach 2.4 HSCT (EI = 15)		Boeing

*Scheduled subsonic fleet emissions are revised to account for flights from HSCTs. Also, NO_x Emission Index (EI) shown applies only to the HSCT fleet in the scenarios; EI for subsonics will be different for each projected aircraft type.

Table 4. Global Emissions Database Requirements

<u>Issue</u>	<u>Criteria</u>
Grid resolution	1° x 1° x 1 km
Documentation	Clear paper trail public domain
Flexibility (to AESA inquiries)	Required
HSCT demand	Held constant for all scenarios
General methodology	Consistent approach
Performance	Realistic climb, cruise, and descent
Seasonality	Evaluate and consider

Table 5. Criteria and Responsibilities in Developing Emissions for the 1990 Fleet

Fuel use
- Document breakdown by
    - OAG/Passenger *Boeing*
    - OAG/Cargo *Boeing*
    - Charter *McDonnell Douglas*
    - USSR/China Civilian *McDonnell Douglas*
    - Military *McDonnell Douglas*
    - Turbine "feeder" aircraft and turboprops *Boeing*

Develop generic aircraft type   *Boeing/McDonnell Douglas*

Flight paths
- Document OAG routes by
    - End points
    - Great circle routes

Aircraft
- Document all major civil aviation aircraft
    - Fuel use
    - Engines: emissions vs. path (Δz, Δl) during takeoff, climb, ...
- Estimate others

Engines
- EI's from known/tested
    EI vs. cycle: takeoff*, climb, cruise, descent
- Estimate EI's from others
    Function of temperature, pressure

* Takeoff is most uncertain, but least important, therefore primarily focus on emissions > 3000 ft

Table 6. Criteria and References in Developing Emissions for the 2015 Subsonic and HSCTs Scenarios

Demand for air travel between city-pairs, number of city-pairs, frequency (location of military flights)   *Boeing/McDonnell Douglas*
Demand scaled up from 1990 based on differential growth of sectors

Subsonic aircraft
- Check against total fuel burn for
  - Scheduled passenger (all OAG type flights)   *Boeing*
  - Cargo   *Boeing*
  - Charter   *McDonnell Douglas*
  - USSR/China (non-OAG flights)   *McDonnell Douglas*
  - Military   *McDonnell Douglas*
  - Turboprops   *Boeing*
- Type of aircraft
  - Seating, speed, turnaround time, flight characteristics
        Boeing/McDonnell Douglas
  - Engines/EI over flight path   *GE/Pratt & Whitney*
  - Routing   *Boeing/McDonnell Douglas*

HSCTs
- HSCT type (Mach #)
  - Different Mach numbers will mean different scenarios
- Number of HSCTs (roughly 500), number of seats per HSCT (300)
- Number of city-pairs for HSCTs (~250), frequency of flights
  Boeing/McDonnell Douglas
- Flight profile, fuel flow, EI
- Routing structure (operational restrictions)

  - A → B   great circle

  - Way points A → A' → B

  - Route is always > great circle

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Table 7. Table of Generic Aircraft Types to Be Used in the Development of Subsonic Scenarios

		Historical (1952-1991)		Forecast (1992-2010)	
TYPE	CATEGORY	MODELS		MODELS	
G1	Short- and Medium-Range <120 Seats	727-100 737-100/-200 Trident-1/2 MD-87 BAe 146 F-100	Caravelle 880 DC-9 BAC 1-11 F-28	737-500 MD-87 BAe 146 BAC 1-11	F-100 DAA-92 DAA-122
G2	Short- and Medium-Range 120-170 Seats	727-200 MD-81/-82/-83/-88 737-300/-400 707-120/-220 DC-8-10/-20	A320 Mercure Trident-3 720	737-300/400 MD-81/-82/-83/-88 MD-90-30 MD-90-50	A319 A320
G3	Short- and Medium-Range 171-240 Seats	757 767-200	A310-200 DC-8-61	757 767-200 A310	A321 MD-90-40
G4	Short- and Medium-Range 241-350 Seats	767-300 DC-10-10/15	L-1011-1 A300	767-300	A300-600
G5	Short- and Medium-Range >350 Seats	747		747SR 747-X 777	A330 MD-12
G6	Long-Range <240 Seats	767-200 707-320/-420 A310-300 DC-8-62/63 DC-8-30/40/50	Concorde VC-10 990 Comet	767-200	A310
G7	Long-Range 241-350 Seats	L-1011-100/-200/-500 DC-10-30/-40 767-300	 747SP	767-300	A340
G8	Long-Range >350 Seats	747 MD-11		747 MD-11 A330 747-X MD-12 A340 777 A350	

Table 8. Priorities for Scenario Development by September 30 Deadline for 1993 Assessment

High Priority

Establish city-pairs and waypoint routing

Mach 1.6 engine emissions (need input from engine companies)

Make HSCT choices as realistic as can (Mach 1.6 criteria different from Mach 2.4)

Passenger demand (demand for number of seats per city-pair) is fixed in scenario development

Scenarios to be developed for a single NO_x EI (other scenario will be scaled)

"Global" (not detailed) treatment of military and turboprop emissions

For 1990 commercial fleet, provide final emissions table only (based on detailed study by Boeing)

Have emissions available on 1° by 1° by 1 km grid

Lower Priority

The Mach 2.0 scenarios (however, try to make available in time for the assessment)

Seasonal variations in the 1993 assessment scenarios (get in 1995 assessment)

Detailed treatment of military and turboprop emissions

Generic aircraft description of 1990 fleet for publication (provide by April 1993)

Determine sulfur content in emissions for both current and future fleets (need for 1995 assessment, but not likely to be ready for 1993)
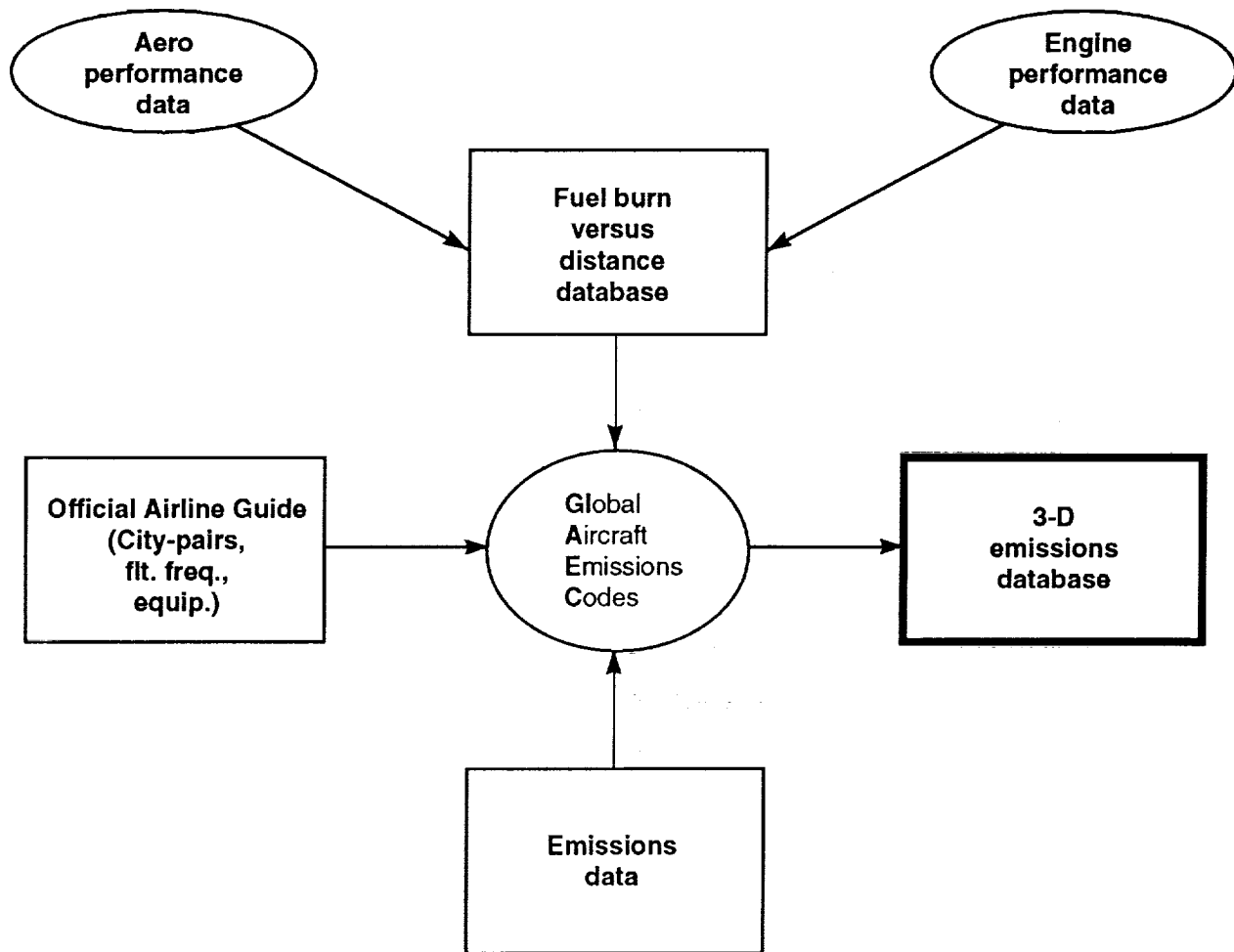
Figure 1. Emissions scenario generation procedure.
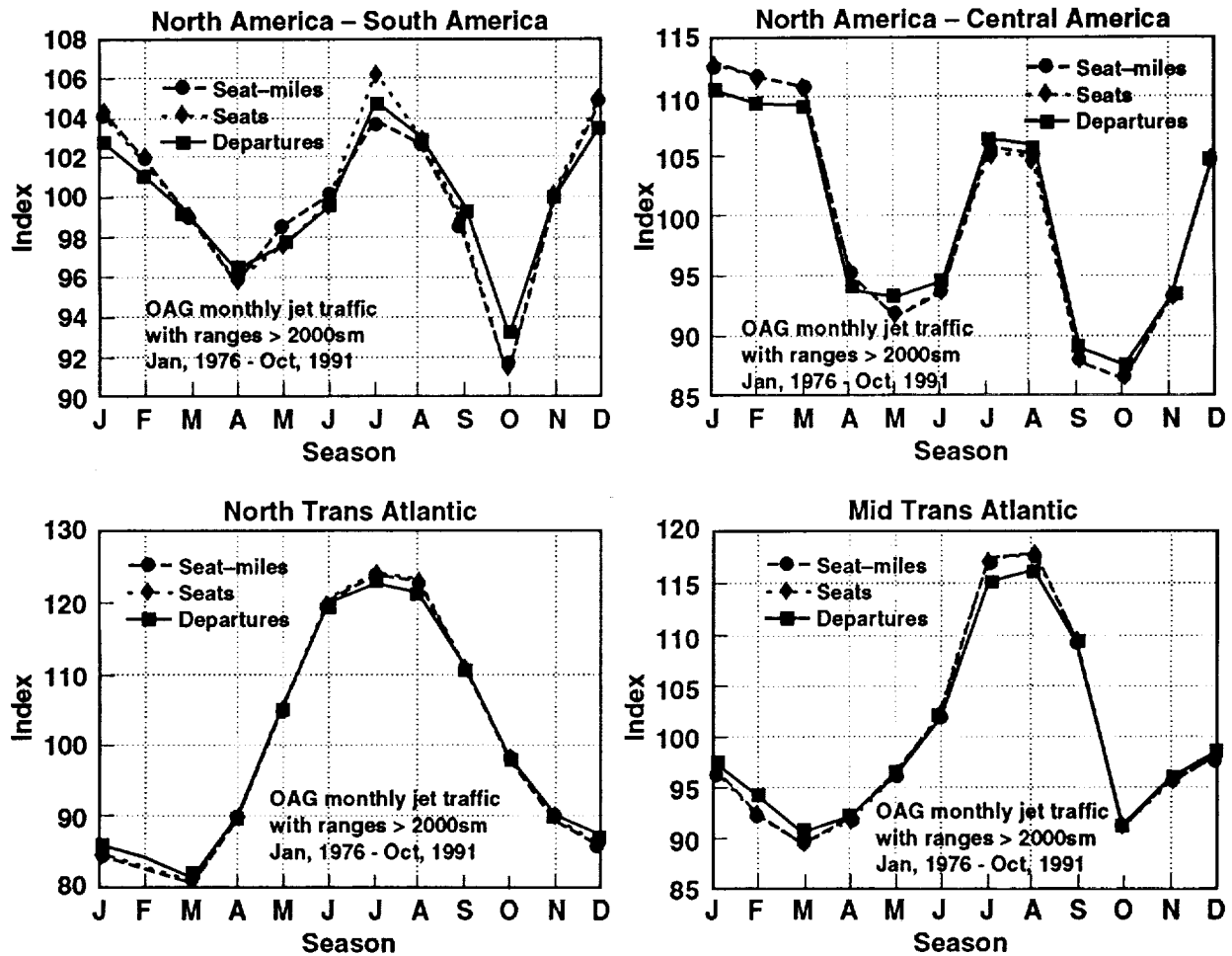
Figure 2. Seasonality analysis for various flight regions, based on analysis of official airline guide data at McDonnell Douglas (Metwally, Personal Communications, 1992).
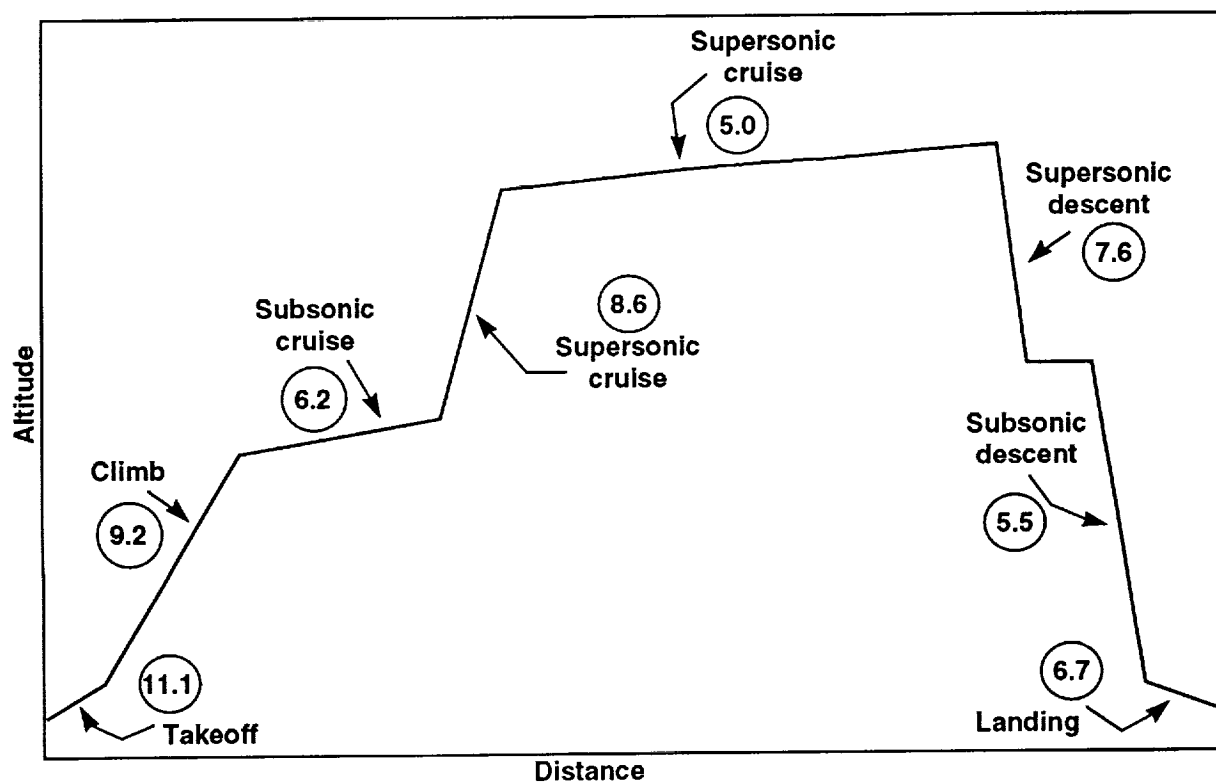
Figure 3a. Schematic of a typical HSCT mission profile and the emission indices (EI) for NO_x emissions, corresponding to a turbine bypass engine incorporating RQL combustion (in circles).
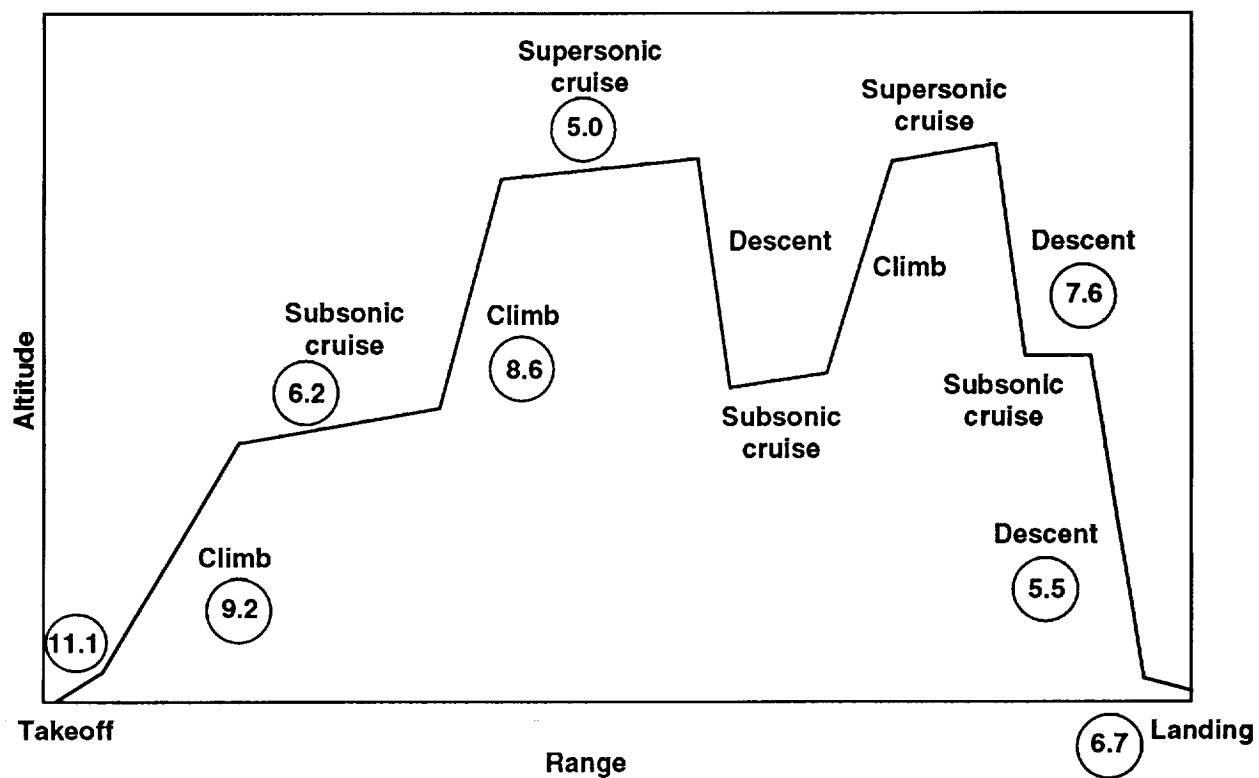
Figure 3b. Schematic for possible mission involving subsonic flight over land in mid-mission.

MACH 1.6

320 FT 8 IN.

163 FT 7 IN

69 FT 2 IN
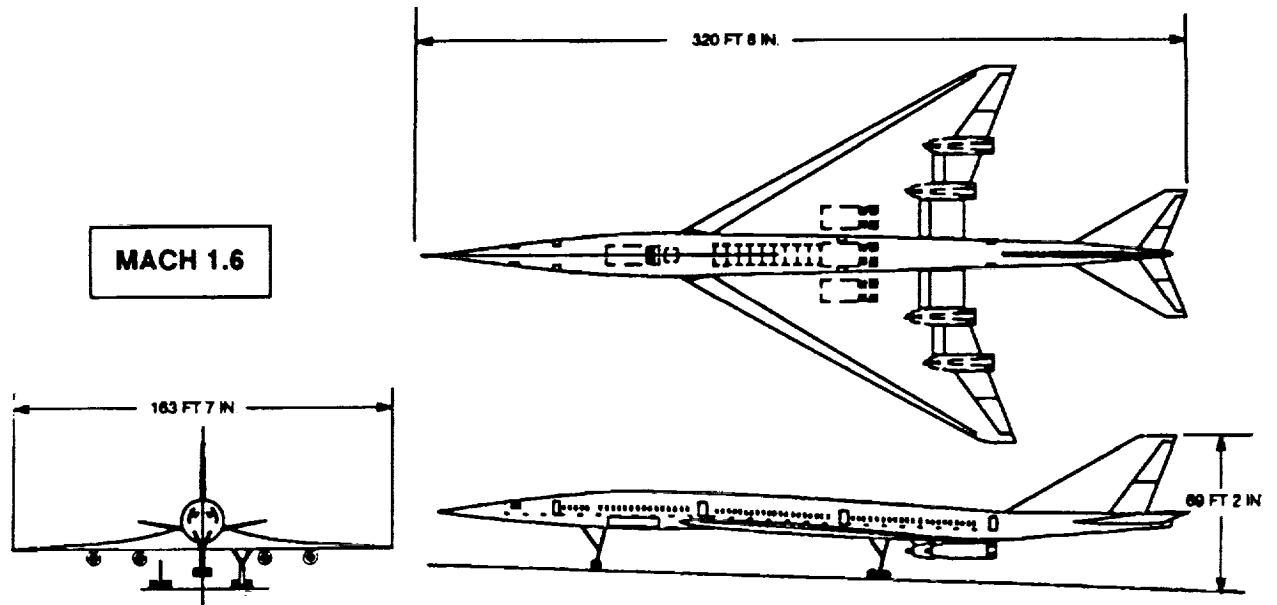
Figure 4a. Configuration for a Mach 1.6 HSCT as developed in prior design optimization studies at McDonnell-Douglas.

Model 1080-920

Span 135 ft

Length = 311 ft
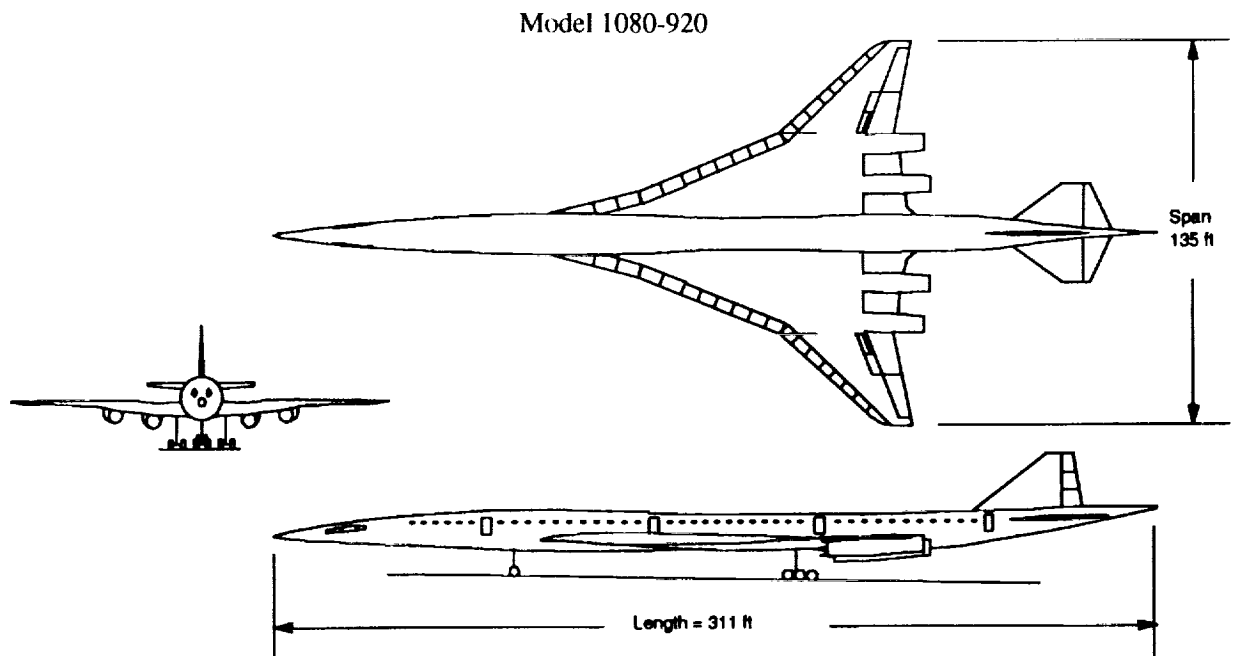
Figure 4b. Configuration for a Mach 2.4 HSCT as developed in prior design optimization studies at Boeing.
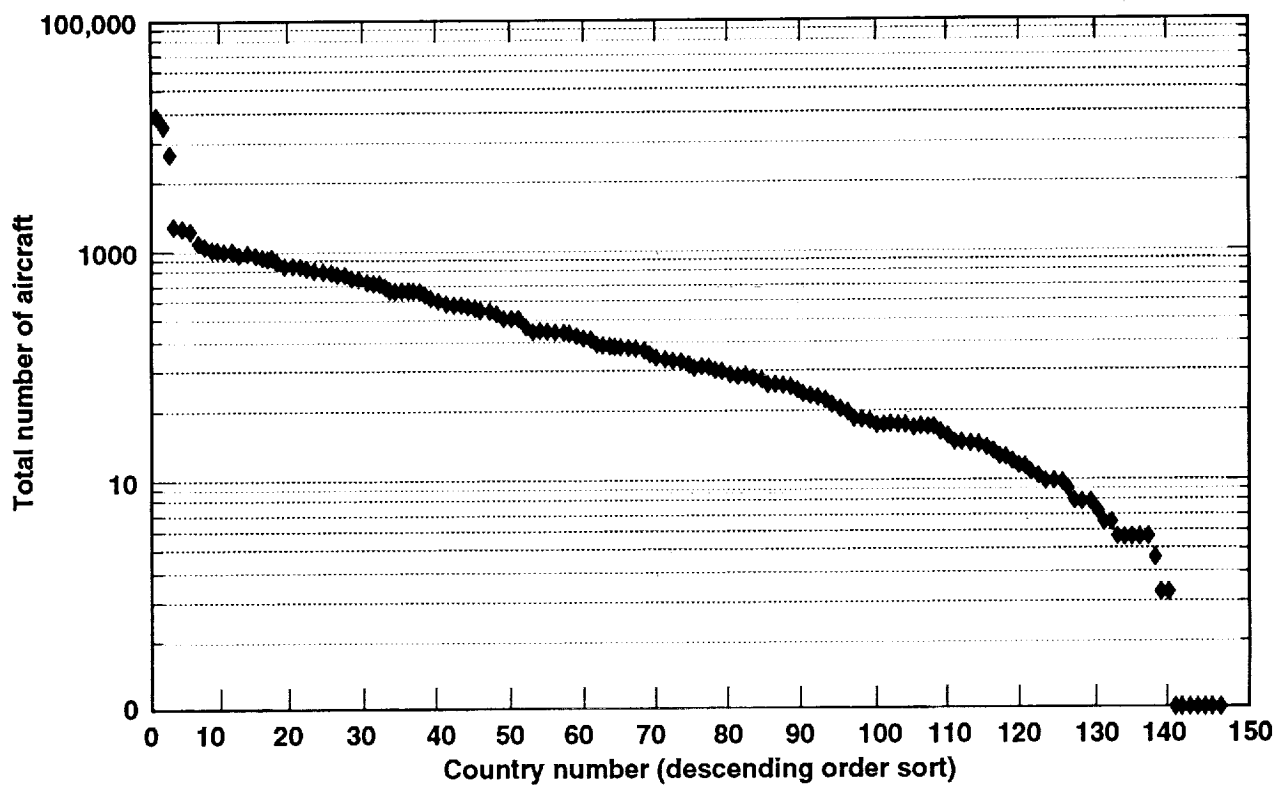
Figure 5. Global distribution of fixed-wing military aircraft.

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Military balance 1989-1990 inventory of aircraft	Mapping considerations	Assignment	
		Type	**Fuel burn multiplier**
A-10	From *Jane's*	A-10A	1.00
A-7	• Number of engines	F-8J	1.00
.	• Thrust per engine	.	.
.	• Engine type (fan, jet, prop, etc.)	.	.
.	• Maximum gross weight	.	.
CM-170	• Performance	A-4M	0.50
F-6	• Vintage	F-4C/D	0.50
PA-34	Subjective assessment	P-3C	0.25

Representative aircraft

A-4M	A-10A	F-111F	C-141A	DC-3/4
AV-8A	F-4C/D/E	C-5A	B-52G	E-4B
F-8J	F-15A/B/C/D	C-130B/H	FB-111A	DC-9
P-3C	F-16A/B	C-135B	KC-10A	

Figure 6. Representative aircraft assignment process.

The chart contains the following data table:

Segment	Cumulative distance (nmi)	Cumulative fuel burn (lb)	Altitude (ft)
Start	0	0	0
Takeoff	5	210	1500
Climb	37	950	25000
Cruise out	270	2680	25000
Descend	300	2726	5000
Combat at target	300	5100	5000
Climb	338	5670	37500
Cruise back	536	6570	38500
Descend/Land	600	7480	0
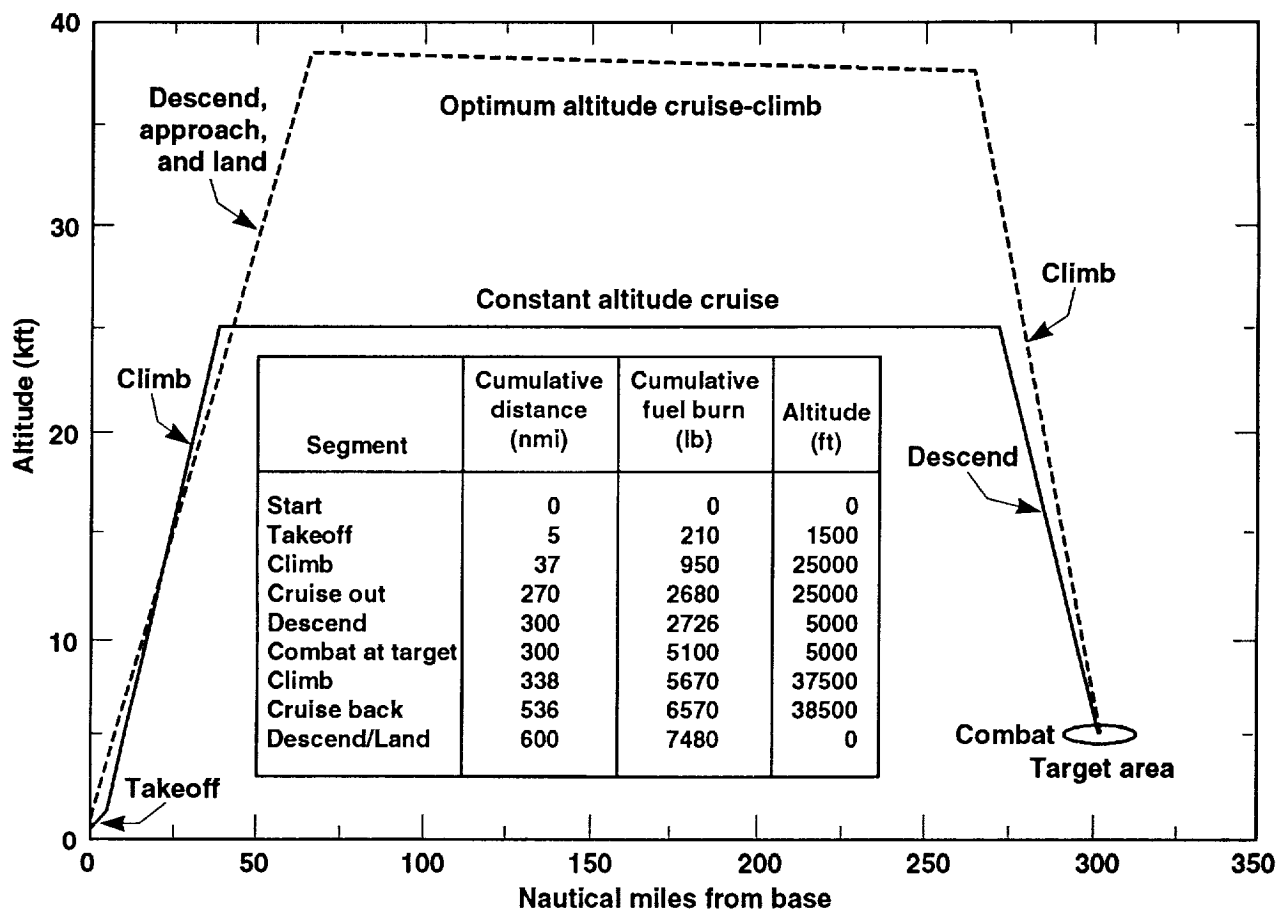
Figure 7. Representative flight plan for the A-4M military aircraft.

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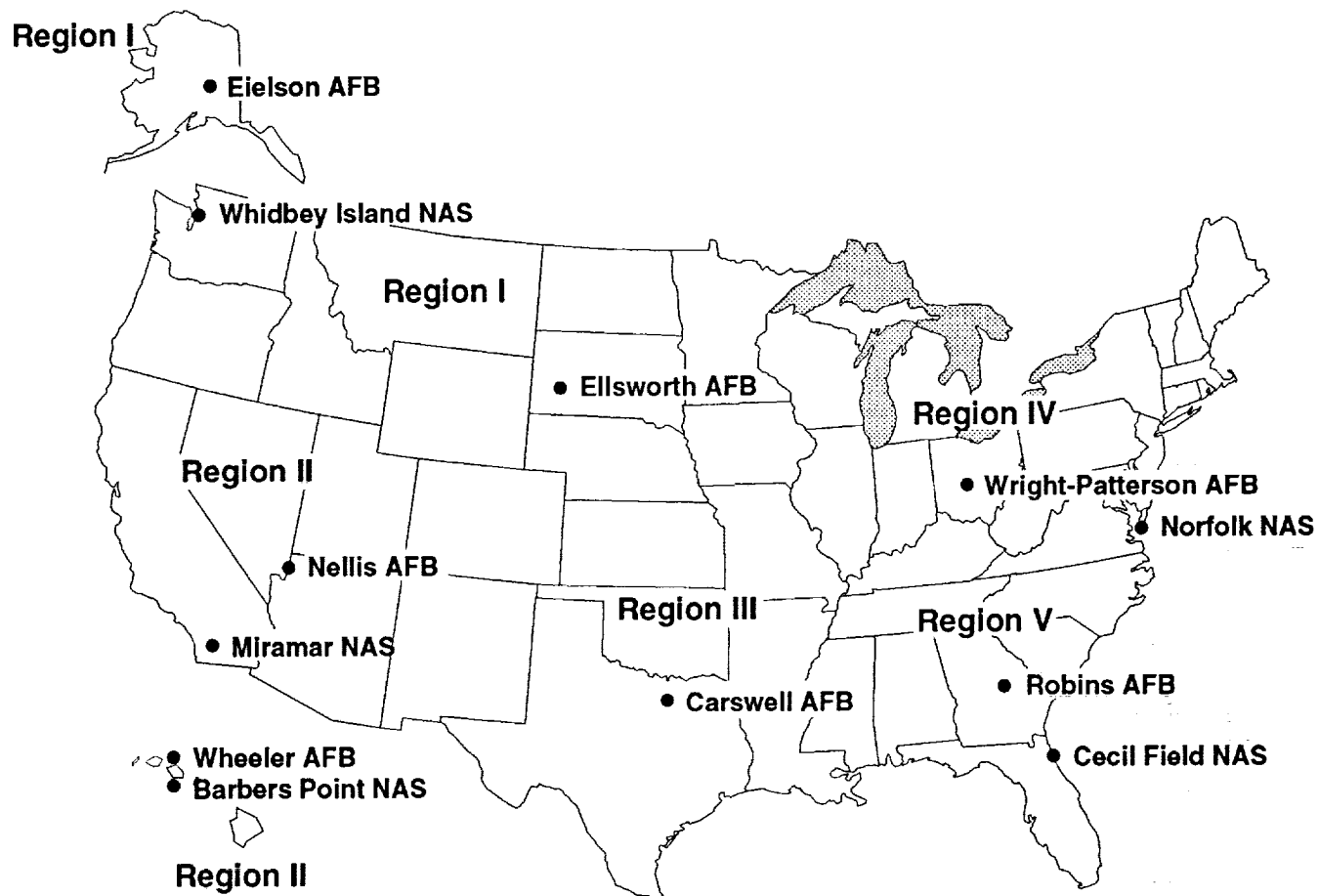
Figure 8. U.S. basing regions selected for representation of military aircraft fleet.
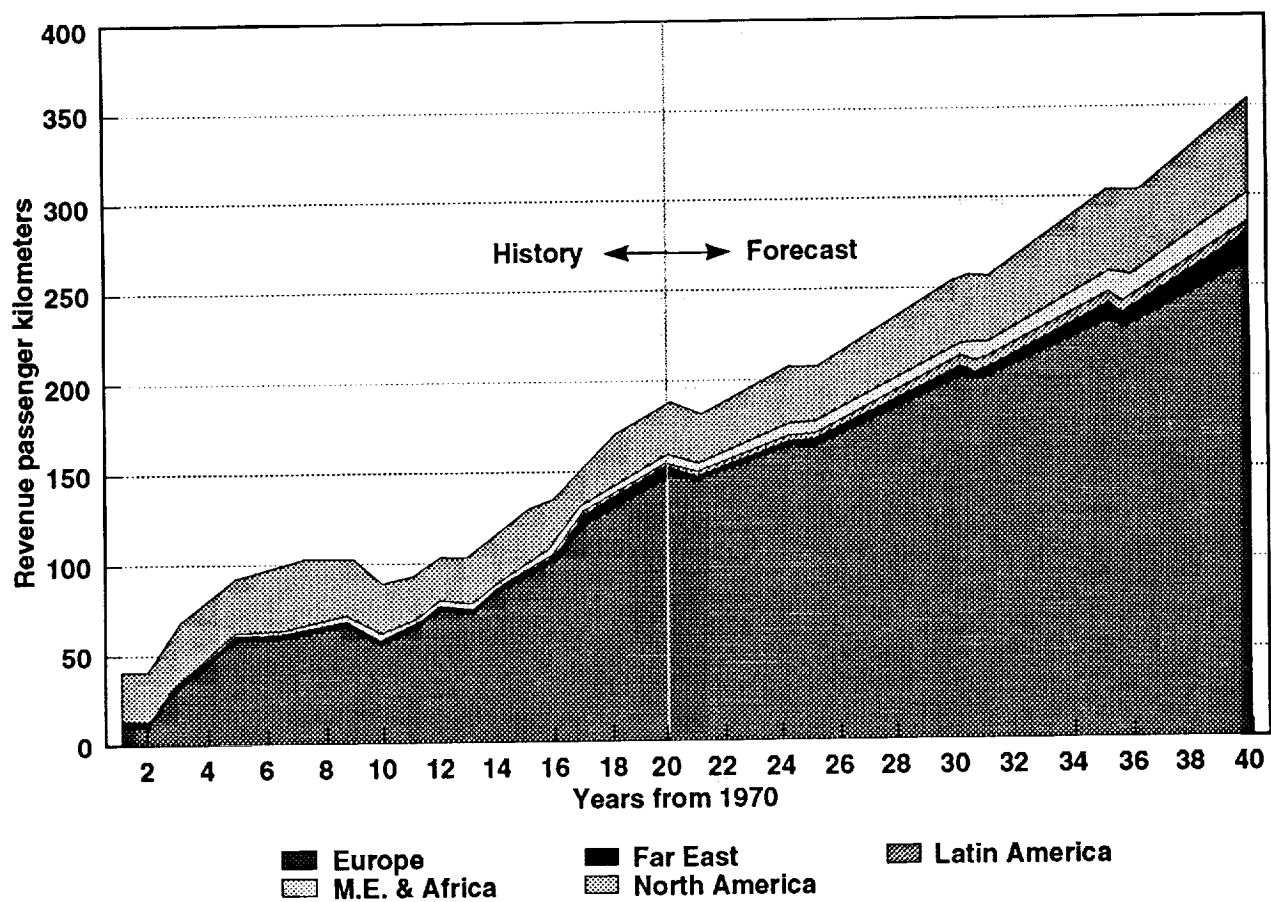
Figure 9. World traffic forecast of nonscheduled (charter) traffic based on ICAO data.
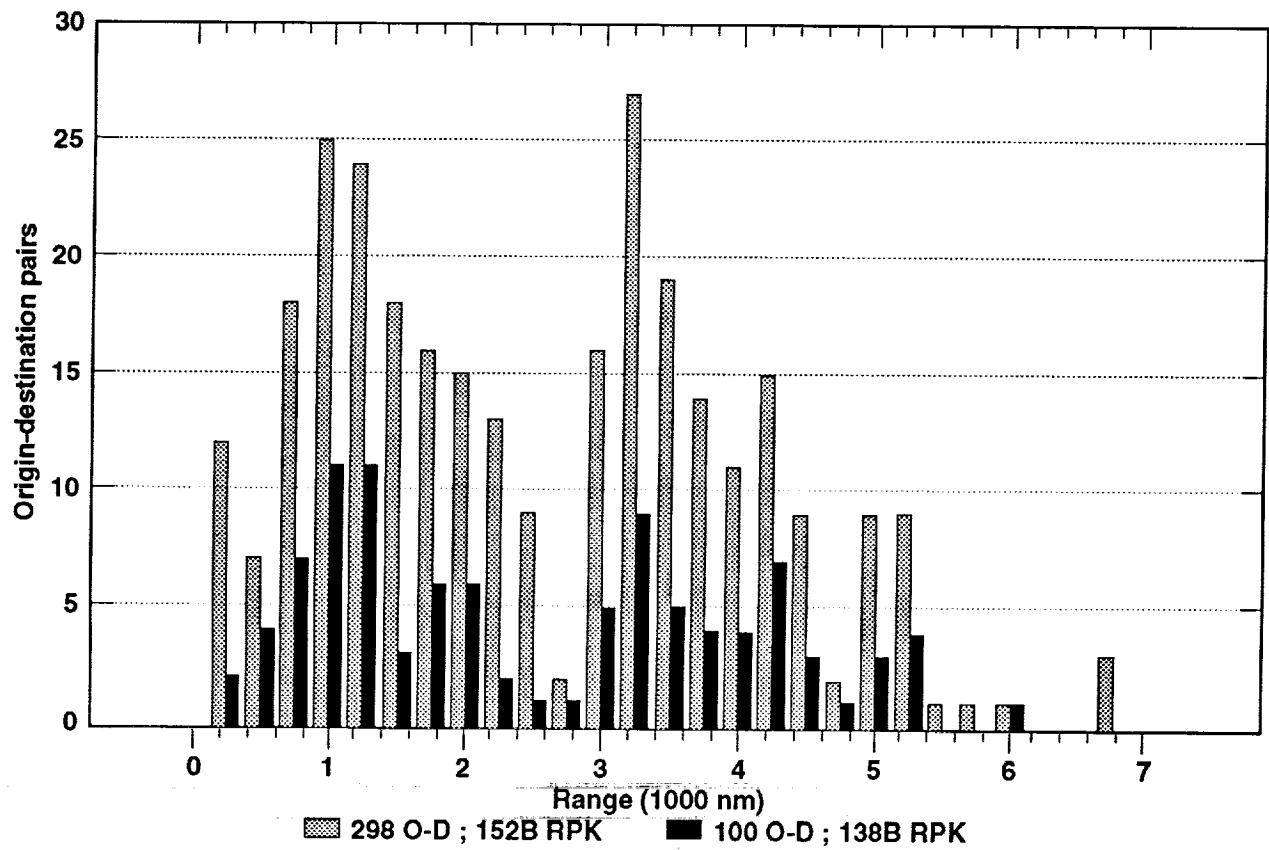
Figure 10. Global distribution by range of charter flights for various origin—distribution (O-D) pairs. Shown in black are the top 100 combinations by Revenue Passenger Kilometers (RPK).

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APPENDIX

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Chapter 3

Heterogeneous Chemistry in the Stratosphere:
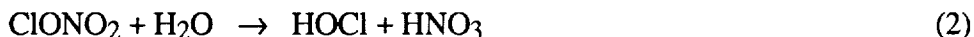# A Review of Laboratory Measurements

Margaret A. Tolbert
University of Colorado
Boulder, CO

INTRODUCTION

There is now general agreement that heterogeneous chemistry -- on both polar stratospheric clouds (PSCs) and the stratospheric sulfate layer -- must be included in stratospheric chemical models used to predict the atmospheric impact of high-speed civil transports (HSCTs). The properties of the stratospheric particulate are summaried in Table 1. For more details, see Turco et al. (1989). Type I and type II PSCs are solid particles composed of nitric acid/ice and water ice, respectively. In particular, type I PSCs are thought to be nitric acid trihydrate (NAT) crystals (Toon et al., 1986; McElroy et al., 1986; Crutzen and Arnold, 1986; Hanson and Mauersberger, 1988a). Because both types of PSCs require quite low temperatures to form, they are found predominantly in the cold polar winters. In contrast, the stratospheric sulfate layer consists of supercooled solutions of concentrated sulfuric acid in water. The acid concentration of the aerosols is dictated by the temperature and the water partial pressure (Steele et al., 1983). If the water pressure is greater than the vapor pressure of water over the sulfuric acid, the droplet will absorb water to maintain equilibrium. For stratospheric temperatures in the range 210 to 240 K, the expected composition of the aerosol is 60 to 80 wt% H_2SO_4. These supercooled aerosols are distributed globally, and dramatically increase in abundance after major volcanic eruptions such as El Chichon (1982) and Pinatubo (1991).

Heterogeneous reactions on stratospheric aerosols have the potential to impact the concentration of trace species that control the O_3 abundance (Solomon, 1988). For example, the following heterogeneous reactions (1-5) on the surfaces of PSCs have been implicated in the photochemical mechanism responsible for the Antarctic "ozone hole."

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3 \tag{1}$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \tag{2}$$

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{3}$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \tag{4}$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O. \tag{5}$$

Reactions (2-5) all convert inert chlorine ($ClONO_2$, HCl) into photochemically active forms (HOCl, Cl_2, $ClNO_2$). Upon photolysis, these molecules form chlorine radicals that participate in catalytic ozone destruction cycles.

Reactions (1-4) all result in nitric acid formation. This leads to "denoxification" or the temporary reduction of NO_x by conversion to HNO_3. Permanent NO_x removal, i.e., "denitrification," can occur if particulate HNO_3 falls out of the stratosphere by PSC sedimentation. A result of denoxification or denitrification is that less NO_x is available for sequestering active chlorine back into inactive forms through, for example, reaction (6):

$$ClO + NO_2 + M \rightarrow ClONO_2 + M. \tag{6}$$

It can therefore be seen that heterogeneous reactions involving only odd nitrogen (i.e., reaction 1) can indirectly affect ClO_x, through coupling reactions such as (6).

In the present review, experimental measurements are summarized for heterogeneous reaction rates on laboratory surfaces that model stratospheric particulate. Although the focus will be on reactions (1-5), other processes, such as heterogeneous chemistry involving HO_x species, will also be considered. In addition to measurements of heterogeneous reaction rates, laboratory studies of trace gas solubility and diffusion in stratospheric aerosol will also be considered.

EXPERIMENTAL TECHNIQUES AND DEFINITIONS

The experimental quantity used to characterize heterogeneous reaction rates is the reaction probability, γ, defined as the fractional collision frequency that leads to reactive loss:

$$\gamma = \frac{\text{\# molecules reacting (molecules sec}^{-1})}{\text{\# gas-surface collisions (collisions sec}^{-1})} \quad . \tag{7}$$

In several laboratory experiments, the number of molecules reacting (or forming) is determined by measurements of gaseous species using mass spectrometric or other techniques. Some experiments also measure the number of reacting molecules by observing the growth of condensed phase species. The number of gas-surface collisions depends on the trace gas pressure and is obtained from gas-kinetic theory as $(<v> [N/V] A)/4$, where $<v>$ is the average velocity (cm sec^{-1}, temperature dependent), N/V is the gas number density (molecules cm^{-3}), and A is the surface area (cm^2). The rate of non-reactive uptake (still denoted γ) is measured in a similar manner but is usually referred to as the "net uptake efficiency."

In addition to measuring heterogeneous reaction probabilities, several experiments measure trace gas solubilities in stratospheric aerosol materials. For liquid solutions, the solubility is given by the Henry's law constant, H (mole l^{-1} atm^{-1}), i.e., the equilibrium constant for reaction (8):

$$M_{(g)} \quad \rightarrow \quad M_{(aq)} \qquad K_{eq} = H . \tag{8}$$
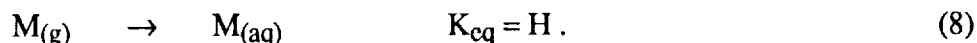
If further reactions of $M_{(aq)}$ occur in solution (e.g., ionization, proton transfer) this can have the effect of increasing the apparent Henry's law constant, usually then referred to as H*. The temperature dependence of the Henry's law constant is given by the Van't Hoff equation:

$$\log H^* = -\Delta H_{sol}/RT + \Delta S_{sol}/R \tag{9}$$

where ΔH_{sol} is the heat of solvation of the dissolving species and ΔS_{sol} is the change in entropy upon solvation. Because ΔH_{sol} normally is negative, the solubility H*, is expected to increase as the temperature is lowered. For convenience, equation (9) is often expressed as log H* $= A/T + B$ where A and B are experimentally determined constants.

Experiments to measure trace gas solubilities and heterogeneous reaction rates have been performed in several laboratories. Slightly different experiments have been used for the study of sulfate versus PSC chemistry; the experimental techniques are summarized in Table 2. For studies of stratospheric sulfate aerosols, experiments have been performed on a large variety of surfaces including submicrometer aerosols (Mozurkewich and Calvert, 1988; A. Fried, personal communication, 1992), 200-μm droplets (Worsnop et al., 1989; Watson et al., 1990; Van Doren et al., 1991), 700-μm-thick films (Hanson and Ravishankara, 1991a) and macroscopic bulk samples (Tolbert et al., 1988a; Reihs et al., 1990; M. Molina, personal communication, 1992). This wide range of experimental techniques and sample dimensions is extremely valuable for understanding heterogeneous processes on stratospheric sulfate aerosols.

For the PSC studies, most of the experiments have been performed on thin film samples ranging from < 1 μm to several hundred μm thick (Molina et al., 1987; Tolbert et al., 1987, 1988b; Leu, 1988a,b; Hanson and Mauersberger, 1988a,b,1990; Leu et al., 1991; Hanson and Ravishankara, 1991b, 1992; Kenner et al., 1992a,b; Abbatt and Molina, 1992a,b). These films are normally prepared by condensation of the appropriate vapors onto a cold surface. Different

conditions, such as the film growth procedure, total gas pressure, and detection procedure, were used in each experiment. Furthermore, in recent work spectroscopy is being used to probe the condensed phase of the PSC material (Tolbert and Middlebrook, 1990; Ritzhaupt and Devlin, 1991; Smith et al., 1991; Koehler et al., 1992a,b).

HETEROGENEOUS PROCESSES ON SULFURIC ACID

Solubility of Trace Species in Sulfuric Acid

The solubilities of HCl and HNO_3 in liquid sulfuric acid solutions have recently been measured by several groups. The effective Henry's law constants are shown for HCl and HNO_3 in Figures 1 and 2, respectively. The data are plotted as a function of temperature according to equation (9). It can be seen that where the data overlap, there is reasonable agreement between the various experiments. The recent low temperature data (Reihs et al., 1990; M. Molina, personal communication, 1992; D. Worsnop, personal communication,1992) extrapolate nicely to room-temperature results (Vandoni, 1944; Watson et al., 1990; Van Doren et al., 1991).

Several general conclusions can be derived from the data in Figures 1 and 2. First, as expected, the Henry's law solubility *increases* with *decreasing* temperature as predicted by equation (9). Second, the solubility *increases* as the concentration of sulfuric acid *decreases*. Both of these factors work together to predict that the highest solubility of HCl and HNO_3 in stratospheric sulfate aerosols will occur at low temperatures, where the sulfate particles will be most dilute.

The magnitude of the measured solubilities deserves note. For 60 - 80 wt% H_2SO_4, representative of the global sulfate layer, the solubility of HCl is exceedingly low. For example, for $H^* = 10^3$ mole l^{-1} atm^{-1}, relevant for 60 wt% H_2SO_4 at 225 K, the measured solubility dictates that approximately 3 HCl *molecules* will be present in an average aerosol particle. However, it should be noted that such low solubility does not rule out condensed phase reactions involving HCl. For example, Burley and Johnston (1992) suggest that HCl could react with nitrosyl sulfuric acid in H_2SO_4 to form ClNO, even given the extremely low HCl solubility in such solutions. Also, the present solubility measurements do not rule out a more substantial *surface* coverage of HCl on the aerosols. However, recent work by Worsnop et al. (personal communication, 1992) has shown that the surface coverage of HCl on 70 wt% H_2SO_4 at 240 K is less than 10^{-4} monolayers.

The nitric acid solubility is also quite low in 60 - 80 wt% H_2SO_4, with stratospheric aerosols having an estimated composition of < 0.05 wt% HNO_3 for 58 wt% H_2SO_4 at 215 K (Reihs et al., 1990). Given the low HNO_3 solubility, heterogeneous reactions on H_2SO_4 producing nitric acid (e.g., reactions 1-4) should produce predominantly gas phase HNO_3.

Recent measurements have also been made of the solubility of HOCl in sulfuric acid (Hanson and Ravishankara, 1992). These authors estimate a solubility of approximately 10^4 M atm^{-1} for HOCl in 60 wt% H_2SO_4 at 205 K. In this work, estimates were also made for the second-order rate coefficients for the reactions of HCl with HOCl and $ClONO_2$. The results suggest that these reactions are not likely to be important on the background stratospheric sulfate layer.

For very low temperatures that might precede PSC formation, it is possible that the sulfuric acid aerosols become quite dilute (before they freeze). Under these conditions the Henry's law solubility of both HCl and HNO_3 are greatly increased (M. Molina, personal communication, 1992). Thus, for 40 wt% H_2SO_4 solutions, the amount of condensed HNO_3 could be quite significant, approaching 10% by weight. Such concentrations could impact the heterogeneous

chemistry, as well as the nucleation of PSCs. Such particles would also absorb much more HCl and could contribute to chlorine activation prior to PSC formation (Wolff and Mulvaney, 1991).

Heterogeneous Reactions on Sulfuric Acid

Because of the low solubility of HCl in concentrated sulfuric acid, heterogeneous reactions on the global stratospheric sulfate layer (60-80 wt% H_2SO_4) are likely to be dominated by processes that do not directly involve HCl. Thus, reactions (1) and (2) will be considered first. The measured probabilities for the water reactions of $ClONO_2$ and N_2O_5 on sulfuric acid are shown in Figures 3 and 4, respectively. Although the data for the $ClONO_2$ reaction (2) are limited, there is excellent agreement. The reaction probability exhibits a very strong dependence on the sulfuric acid concentration, with dramatically lower probabilities for more concentrated solutions. Hanson and Ravishankara (1991a) have fitted the data to the curve $\log_{10}(\gamma) = 1.86 - (0.0747)W$, where W is the wt% acid concentration. It should be noted that the bulk data shown (Golden et al., 1992) differ by approximately a factor of 2 from earlier data (not shown) on this reaction from Tolbert et al. (1988a). However, the sulfuric acid solutions used in Tolbert et al. (1988a) were not titrated to verify their composition. Owing to the large dependence of γ on wt% H_2SO_4, small errors in the solution concentration could easily account for the factor of 2 difference between the earlier and present results on bulk solutions.

Given the above dependence on wt% H_2SO_4, reaction (2) is unlikely to be important for background conditions of stratospheric aerosol. However, under volcanic aerosol conditions where the aerosol surface area is greatly elevated, this reaction could begin to play a role in ClO_x and NO_x partitioning. Furthermore, because the concentration of sulfate aerosols decreases at low temperatures, reaction (2) will assume increasing importance at high latitudes where colder temperatures are achieved.

The reaction of N_2O_5 with H_2O on sulfuric acid (reaction 1) has been studied by a large number of groups using several different techniques. In contrast to the $ClONO_2$ reaction, N_2O_5 appears to react readily on liquid sulfuric acid solutions under almost all conditions. For example, the data in Figure 4 cover a range of sulfuric acid concentrations from 40 to 95 wt% H_2SO_4 and temperatures from 215 to 293 K. The reaction probability appears to have little dependence on either temperature or wt% H_2SO_4. It is thus likely that this reaction plays a major role in the NO_x partitioning in the stratosphere. Through coupling between the NO_x and ClO_x families (e.g., reaction 6), reaction (1) on sulfuric acid can indirectly cause an increase in the ratio of active to inactive chlorine. Thus, it is essential that reaction (1) be included in atmospheric models assessing the impact of stratospheric aircraft.

As discussed above, the solubility of HCl in sulfuric acid solutions is quite low. Nonetheless, laboratory experiments have shown that reactions (3) and (5) are possible for very large pressures of HCl. For example, Tolbert et al. (1988a) observed Cl_2 evolution from the interaction of $ClONO_2$ with HCl/H_2SO_4 mixtures, but did not observe an increase in the overall reaction probability. Similarly, Hanson and Ravishankara (1991a) have observed reactions (3) and (5) for elevated pressures of the reactant gases. Thus, although it is possible to force these reactions to occur in the laboratory using high pressures, the results suggest that reactions (3-5) are unlikely to occur on the global stratospheric sulfate layer. Of course, such reactions may yet play a role in chlorine activation for very cold temperatures just slightly preceding PSC formation thresholds. In this case, substantial HCl absorption may occur, making HCl reactions such as (3), (4), and (5) more favorable.

In addition to reactions involving NO_x and ClO_x reservoir species, new laboratory data suggest that heterogeneous reactions of HO_x species may occur on stratospheric sulfate aerosols. For example, Figure 5 shows the reaction probability for formaldehyde on sulfuric acid as a function of wt% H_2SO_4 (Tolbert et al., 1992). Because formaldehyde, CH_2O, is a reservoir for HO_x, any

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heterogeneous loss of formaldehyde could result in a net decrease in HO_x. In contrast to reactions (1) and (2), the formaldehyde uptake *increases* as the sulfuric acid concentration *increases*. Under laboratory conditions, the formaldehyde uptake appears to be irreversible. However, saturation could occur in the atmosphere because of the limited aerosol volume available. Still, the uptake of formaldehyde by sulfuric acid aerosols could substantially alter the chemical composition (and perhaps reactivity) of the aerosols themselves.

Recent laboratory work has also shown that other HO_x species may undergo heterogeneous reactions on sulfuric acid surfaces. Although early work indicated that OH radicals were not readily taken up by 96 wt% H_2SO_4 (Baldwin and Golden, 1980), more recent work (Gershenzon et al., 1987) showed a very rapid uptake, with γ of order unity. Furthermore, Hanson et al. (1992) have shown that both OH and HO_2 are readily taken up by 28 wt% H_2SO_4 at 249 K, with measured uptake efficiencies of >0.08 and >0.05, respectively. Therefore, it appears that heterogeneous chemistry involving HO_x and HO_x reservoirs may be important on stratospheric sulfate aerosols.

Finally, it has recently been suggested (Burley and Johnston, 1992) that sulfuric acid itself may undergo condensed phase reaction to form reactive species in solution. That is, nitrosyl sulfuric acid ($NOHSO_4$) could form in sulfuric acid aerosols under stratospheric conditions, and once formed, could react with HCl to form ClNO, thus providing a new route for chlorine activation by stratospheric sulfate aerosols. Experiments are needed on this system to test these ideas.

Outstanding Issues in Sulfate Chemistry

Although a great deal has been learned over the past five years regarding heterogeneous chemistry on the stratospheric sulfate layer, several lingering questions must be resolved before such chemistry can confidently be included in atmospheric chemical models. Some of these issues are outlined below:

1. *Missing chemistry.* For example, what reactions other than (1-5) might be possible on the stratospheric sulfate aerosol?

2. *Ternary and higher systems.* What is the effect of multiple species dissolved in sulfuric acid? Are there synergistic effects?

3. *Accumulation of trace species in aerosols.* If so, how might the chemistry be impacted? For example, what role might reactions involving $NOHSO_4$ or CH_2O play in sulfate chemistry? Will accumulation of trace species lead to saturation in stratospheric aerosols that may not be evident in the laboratory?

4. *Reactivity of frozen vs liquid H_2SO_4.* What is the impact on heterogeneous reactivity of freezing the sulfuric acid? Hanson and Ravishankara (1991a) found that neither reaction (2) nor (3) occurred on frozen 60 wt% H_2SO_4 at 213 K. However, investigations on frozen sulfuric acid surfaces are quite limited.

5. *Freezing of sulfate aerosols.* How does the freezing of H_2SO_4 aerosols depend on chemical properties such as trace additives? How might soot from the HSCT affect the freezing of stratospheric sulfate aerosols?

6. *Nucleation of PSCs.* What is the role of sulfuric acid aerosols in the nucleation of PSCs? How does the phase of the sulfuric acid (i.e., liquid versus solid) affect nucleation?

HETEROGENEOUS PROCESSES ON PSC SURFACES

One of the primary differences between solid PSCs and liquid sulfuric acid aerosols is the condensed-phase diffusion coefficient. Rapid diffusion in liquids (10^{-5} cm^2 sec^{-1}) tends to distribute trace species throughout the bulk. Thus, in addition to measurement of the reaction probability, γ, it is necessary to measure the trace gas solubilities, H*, and condensed phase reaction rates. In contrast, diffusion through solids is quite slow. Estimates for the diffusion coefficient of trace species in ice fall in the range 10^{-10} to $<10^{-13}$ cm^2 sec^{-1} (Wolff et al., 1989; Chu and Leu, 1992; Koehler et al., 1992b). It is thus likely that for PSCs, the chemistry is dominated by processes that occur on the *surface*. Note, however, that the concept of a PSC *surface* is perhaps somewhat different than the conventional view. Recent measurements of the sticking and evaporation coefficient of water on ice by Haynes et al. (1992) have revealed that ice surfaces in the stratosphere are very dynamic in nature. These workers found that for ice at 200 K, the surface was in a "dynamic equilibrium," with layers evaporating and reforming at a microscopic rate of 500 monolayers sec^{-1}. This may actually allow trace species to become partially "buried" in the surface layer and thus, in the strictest sense, allows more than the surface to participate in heterogeneous chemistry. The dynamic nature of PSC surfaces emphasizes the importance of performing laboratory studies under conditions relevant for the stratosphere to best mimic actual conditions.

Heterogeneous Reactions of ClONO$_2$ and N$_2$O$_5$ with H$_2$O on PSC Surfaces

Since 1987, there have been numerous measurements of the probabilities for the water reactions of ClONO$_2$ and N$_2$O$_5$ on ice surfaces; these are summarized in Table 3. Until recently, there was a significant discrepancy (an order of magnitude) in the results from various laboratories. The discrepancy was resolved when it was recognized that surface saturation might have been affecting the early experimental measurements (Hanson and Ravishankara, 1991b). Surface saturation with HNO$_3$ converts the ice surfaces to nitric acid/ice surfaces, perhaps in the form of NAT. Thus, many of the early experiments were actually measuring the heterogeneous reaction rates of ClONO$_2$ and N$_2$O$_5$ on NAT surfaces. Recent experiments using lower trace gas pressures have led to more consistent values for the heterogeneous reaction probabilities. In short, both reactions (1) and (2) are quite rapid on pure ice surfaces. However, the reaction probabilities are considerably lower on NAT surfaces thought to be representative of type I PSCs. In fact, recent work by Leu et al. (1991) and Abbatt and Molina (1992b) have shown that the reaction probabilities on NAT are a strong function of the available water in the NAT. Both of these authors found that the probability for reaction (2) decreases two orders of magnitude in going from "water-rich" NAT to pure, stoichiometric NAT.

Just as surface saturation can cause NAT "poisoning" in the laboratory, so too might surface saturation occur in the atmosphere. Thus, although type II PSCs are predominantly composed of water-ice, a thin NAT layer may rapidly form on the particle due to heterogeneous reactions forming HNO$_3$. If so, then the reactivity of type II PSCs would probably be similar to that of type I PSCs, because of the similar *surface* characteristics. As mentioned above, reactions (1) and (2) on such surfaces occur only slowly.

Heterogeneous Reactions Involving HCl on PSC Surfaces

The interaction of HCl with PSC materials has been the subject of considerable controversy since it was proposed that chlorine activation on PSCs could provide a mechanism for the Antarctic ozone hole (Solomon et al., 1986). Since 1988, there have been numerous investigations of this system (Hanson and Mauersberger, 1988b; Wofsy et al., 1988; Wolff et al., 1989; Hanson and Mauersberger, 1990; Moore et al., 1990; Leu et al., 1991; Marti et al., 1991; Abbatt et al., 1992; Chu and Leu, 1992; Hanson and Ravishankara, 1992; Koehler et al., 1992b; Molina, 1992). The emphasis of these studies ranged from measurements of bulk HCl solubility in PSC materials to

measurements of the HCl surface concentration. Although there were large differences in the laboratory data initially, a consistent picture of HCl uptake and partitioning in model PSCs has emerged during the last year.

The laboratory data indicate that for high HCl pressures, large uptake occurs on both ice and NAT surfaces. This large uptake is now thought to be due to either surface melting or HCl-hydrate formation. In either case, the HCl is not confined to the surface layers, but diffuses readily throughout the bulk. At low HCl pressures, representative of those expected in the stratosphere, the HCl uptake is much more limited. In fact, recent studies have shown that monolayer to submonolayer coverage of HCl on PSCs is obtained (Hanson and Ravishankara, 1992; Abbatt et al., 1992; Chu and Leu, 1992). However, the uptake of monolayer coverages occurs quite rapidly (Abbatt et al., 1992; Hanson and Ravishankara, 1992), and thus any surface HCl undergoing reaction could be quickly replenished from the gas phase. A main point is that adsorbed HCl on the surface is readily available for heterogeneous reaction with other trace species, e.g., reactions (3-5).

Measured probabilities for reactions (3-5) on PSC surfaces are summarized in Table 4. It can be seen that where the data overlap, there is excellent agreement. Reactions (3) and (5) appear to be very efficient on ice and NAT, and can thus provide a mechanism for activating chlorine when PSC temperatures are achieved in the stratosphere. There is considerably less data for reaction (4) on PSC surfaces, but the reaction apparently is much less efficient. Thus, the main heterogeneous loss path for N_2O_5 in the stratosphere most likely is reaction (1) on sulfuric acid aerosols, as discussed above.

Other Heterogeneous Reactions on PSCs

There have recently been several studies of heterogeneous reactions other than (1) through (5) on PSC surfaces. These include such systems as O_3 (Dlugokencky and Ravishankara, 1992), CF_2O (Hanson and Ravishankara, 1991c), ClO (Kenner et al., 1992a), and PAN and CH_3COOH (R. Friedl, personal communication, 1992). With the exception of CH_3COOH, these studies have revealed rather small reaction probabilities. Thus, heterogeneous reactions of these particular species on PSCs do not appear to be important. However, the list of reactions studied to date is far from comprehensive.

Outstanding Issues in PSC Chemistry

Many of the controversies surrounding PSC chemistry have been resolved in the past few years. From laboratory, field, and modeling data, it is now clear that PSC chemistry has the potential to alter the chemical composition of our atmosphere in ways not thought possible 10 years ago. Although many fundamental issues have been addressed, a microscopic understanding of PSC chemistry is still lacking. Several outstanding questions are addressed.

1. *Are we certain that type I PSCs are NAT?* If so, what type of NAT? [Possibilities include amorphous NAT (Hanson, 1990), a-NAT or b-NAT (Koehler et al., 1992a), and water- or HNO_3-rich NAT (Molina, 1992)]. How will future changes in NO_x and H_2O affect the composition of PSCs?

2. *How do type I PSCs nucleate?* What is the effect of foreign matter (e.g., soot) on PSC nucleation? This is critical to predicting when and where PSCs form and future trends in PSC chemistry.

3. *How does substrate porosity affect PSC chemistry?* Porous substrates have been shown to be present in some of the laboratory data (Keyser et al., 1991) and porosity must be considered in analyzing these data. The morphology of actual PSCs is still uncertain.

4. *Are there additional chemical reactions that could occur on ice and NAT?*

5. *How much of the PSC volume participates in heterogeneous chemistry?* Is it truly a surface phenomenon, or do several, or even hundreds, of layers play a role? How might this impact such processes as chlorine activation and denitrification?

ACKNOWLEDGMENTS

Table 1. Properties of Stratospheric Particulate

Composition	Form	Size (μm)	Temp (K)	Location	Source/Area
60-80 wt%H_2SO_4 (could be as low as 40 wt%H_2SO_4)	liquid (perhaps solid also)	0.01-1	195-240	global	OCS (1 $\mu m^2/cm^3$) Volcanoes (100 $\mu m^2/cm^3$) Aircraft (S in fuel?)
HNO_3/H_2O (approx 50/50 wt%) (Type I PSC)	solid	0.3-3	<195	polar winter	(1 $\mu m^2/cm^3$) N_2O Aircraft (NO_x?)
H_2O/ice (Type II PSC)	solid	1-100 (up to 1000 for wave clouds)	<187	polar winter	(10 $\mu m^2/cm^3$) H_2O,CH_4

Table 2. Laboratory Techniques for Sulfate and PSC Chemistry

Experiment	Model Aerosol Dimension	Total Pressure	Location	References
Sulfate Chemistry				
Flow tube	60-250 nm	≈ atm	NCAR	Mozurkewich and Calvert, 1988 A. Fried, personal communication, 1992
Flow tube	200 μm	2-50 Torr	BC/Aerodyne	Worsnop et al., 1989 Watson et al., 1990 Van Doren et al., 1991
Flow tube	700 μm flowing film	0.5-2 Torr	NOAA	Hanson and Ravishankara, 1991a
Knudsen cell	1 cm	< 10^{-3} Torr	SRI MIT	Tolbert et al., 1988a Reihs et al., 1990 M. Molina, personal communication, 1992

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Table 2. (cont.)

Experiment	Model Aerosol Dimension	Total Pressure	Location	References
PSC Chemistry				
Flow tube	2-10 μm	0.5-1 Torr	MIT	Molina et al., 1987 Abbatt and Molina, 1992*a,b*
Flow tube	13-250 μm	0.3-2 Torr	JPL	Leu, 1988*a,b* Leu et al., 1991
Flow tube	1-50 μm	0.2-2 Torr	NOAA	Hanson and Ravishankara, 1991*b*, 1992
Flow tube	1-124 μm	0.2-1.5 Torr	CSIRO	Kenner et al., 1992*a,b*
Knudsen cell	μm-bulk	$<10^{-3}$ Torr	SRI	Tolbert et al., 1987,1988*b* Quinlan et al., 1990
"Static" cell	≈ 1μm	10^{-6}-10^{-7} Torr	Minnesota	Hanson and Mauersberger, 1988*a,b*, 1990 Marti et al., 1991
FTIR chamber	0.02-20μm	10^{-4} to 10^{-7} Torr	CU Oklahoma State JPL	Tolbert and Middlebrook, 1990 Koehler et al., 1992*a,b* Ritzhaupt and Devlin, 1991 Smith et al., 1991

Table 3. Reaction Probabilities for Reactions (1) and (2) on PSC Surfaces

	ClONO$_2$			N$_2$O$_5$	
Reference	Ice	'NAT'	Reference	Ice	'NAT'

Values that may reflect surface saturation and/or melting:

Reference (ClONO$_2$)	Ice	'NAT'	Reference (N$_2$O$_5$)	Ice	'NAT'
Molina et al., 1987	(0.02)		Tolbert et al., 1988b	(>0.001)	
Tolbert et al., 1987	(0.009)		Leu, 1988b	(0.028)	
Leu, 1988a	(0.06)		Quinlan et al., 1990	(0.03)	(0.015)

More recent measurements:

Reference (ClONO$_2$)	Ice	'NAT'	Reference (N$_2$O$_5$)	Ice	'NAT'
Moore et al., 1990		0.02[a]			
Leu et al., 1991		0.001[a]			
Hanson and Ravishankara, 1991b	0.3	0.006	Hanson and Ravishankara, 1991b	0.024	
Abbatt and Molina, 1992b	>0.02	0.001-.002[a]	Kenner et al., 1992b	0.01-.02	0.0006

[a]Value on "water-rich" NAT. Values on "pure" NAT are considerably lower.

Table 4. Probabilities for Reactions (3-5) Involving HCl on PSC Surfaces

	Ice	'NAT'
$ClONO_2 + HCl$		
Molina et al., 1987	0.05 - 0.1	
Leu, 1988*a*	0.06-0.3	
Moore et al., 1990		0.06-1.0
Leu et al., 1991		0.1
Hanson and Ravishankara, 1991*b*	a	0.3
Abbatt and Molina, 1992*b*	>0.2	>0.2[b]
$N_2O_5 + HCl$		
Tolbert et al., 1988*b*	>0.003	
Leu, 1988*b*	0.05	
Hanson and Ravishankara, 1991*b*	a	0.0032
$HOCl + HCl$		
Hanson and Ravishankara, 1992	>0.3	0.1
Abbatt and Molina, 1992*a*	0.16-0.24	0.17[b]

[a]No enhancement in g was observed over reaction on pure ice without HCl (see Table 3).
[b]Value on "water-rich"-NAT. Value is two orders of magnitude lower for "HNO$_3$-rich"-NAT.
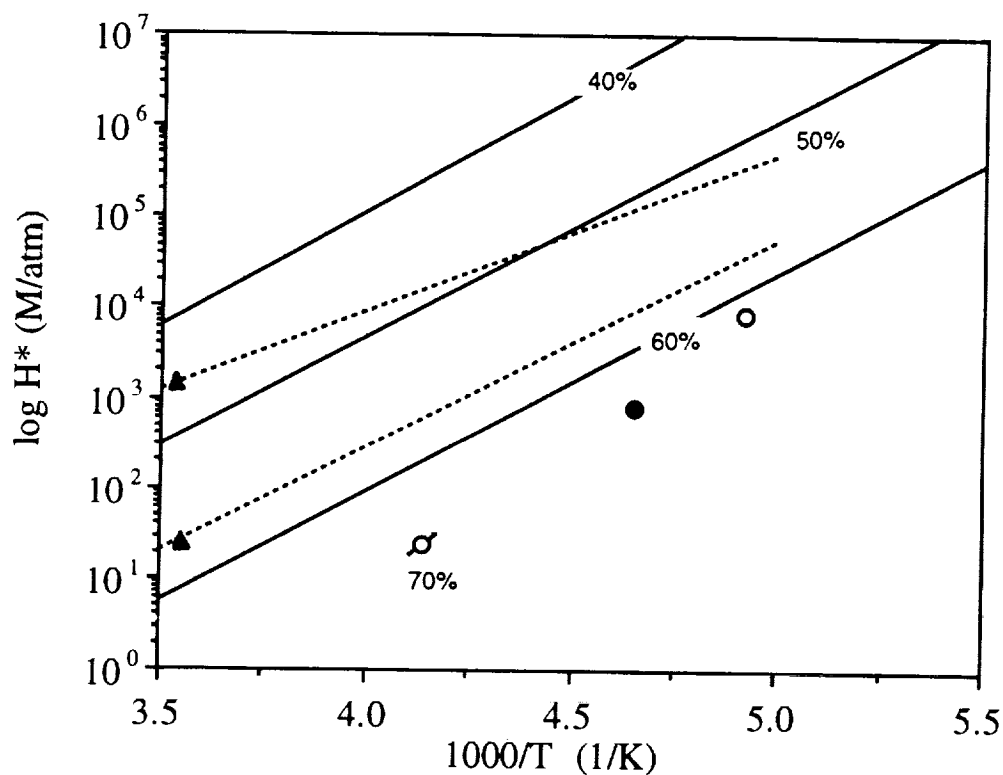
Figure 1. Temperature dependence for the effective Henry's law constant for HCl in 40, 50, 60, and 70 wt% sulfuric acid. (————, M. Molina, personal communication, 1992; ---------- and -O-, D. Worsnop, personal communication, 1992; ●, Hanson and Ravishankara, 1991a, 60 wt%; O, M. Tolbert, personal communication, 1990, 60 wt%; ▲, Watson et al., 1990).
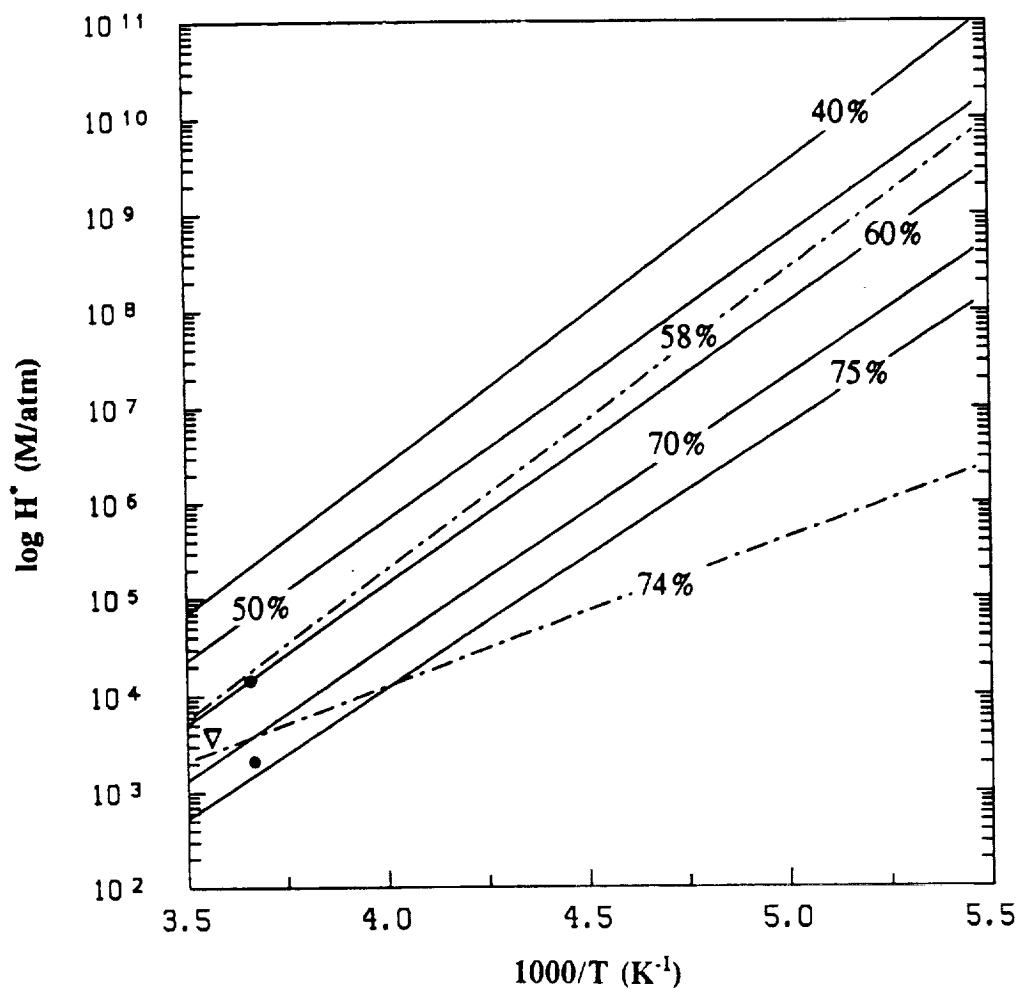
Figure 2. Temperature dependence for the effective Henry's law constant for HNO₃ in 40, 50, ≈60, 70, and ≈75 wt% sulfuric acid. (————, M. Molina, personal communication, 1992; --•--•--•--, Reihs et al., 1990; ∇, Van Doren et al., 1991; ●, Estimated from data in Vandoni (1944) for 58 and 74 wt% solutions).
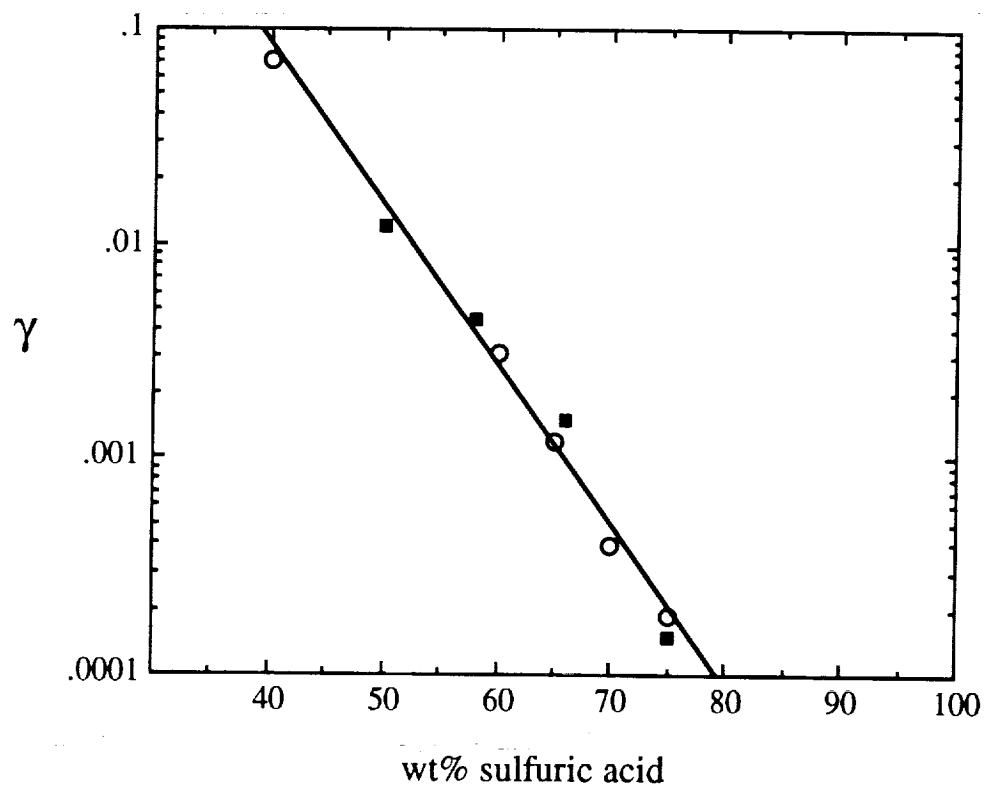
Figure 3. Variation in the reaction probability for the reaction of ClONO$_2$ with water on sulfuric acid as a function of acid concentration. (■, Hanson and Ravishankara, 1991a; Ö, Golden et al., 1992).
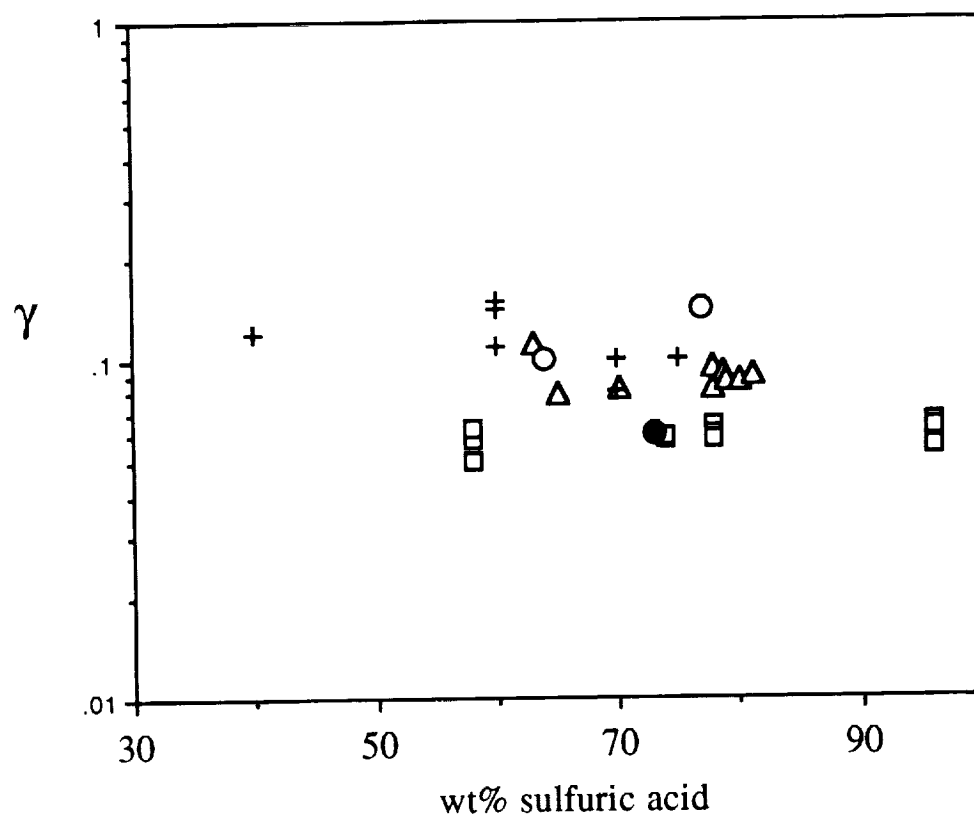
Figure 4. Variation in the reaction probability for the reaction of N_2O_5 with water on sulfuric acid as a function of acid concentration. (+, 215-250 K, Hanson and Ravishankara, 1991a ; Δ, 273 K, A. Fried, personal communication, 1992; ▢, 220-300 K, Golden et al., 1992; ●, 283 K, Van Doren et al., 1991; O, 274-293 K, Mozurkewich and Calvert, 1988).
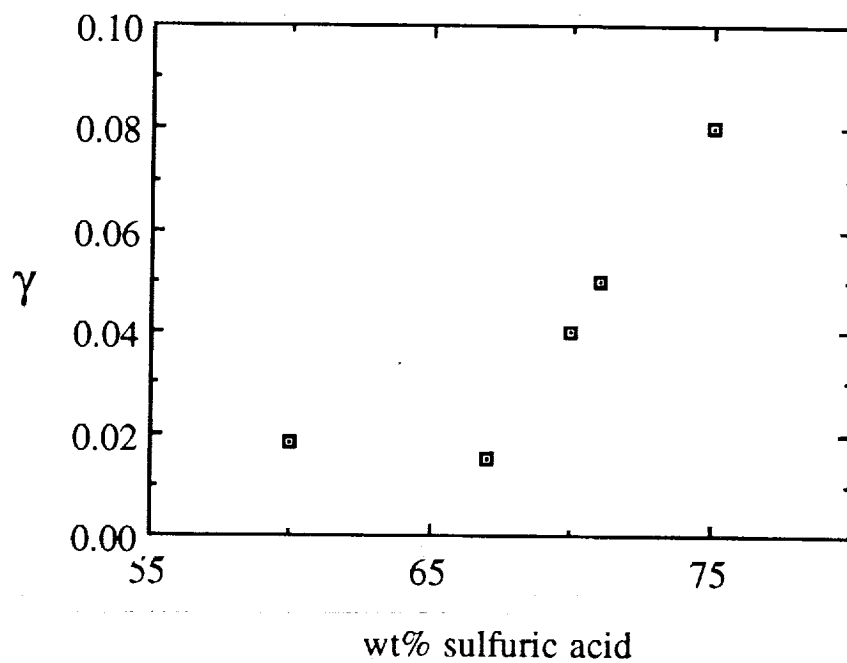
Figure 5. Variation in the reaction probability for the uptake of formaldehyde by sulfuric acid as a function of acid concentration. Data from Tolbert et al., 1992.

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Chapter 4

Stratospheric Tracers and Transport

Alan Plumb
Massachusetts Institute of Technology
Cambridge, MA
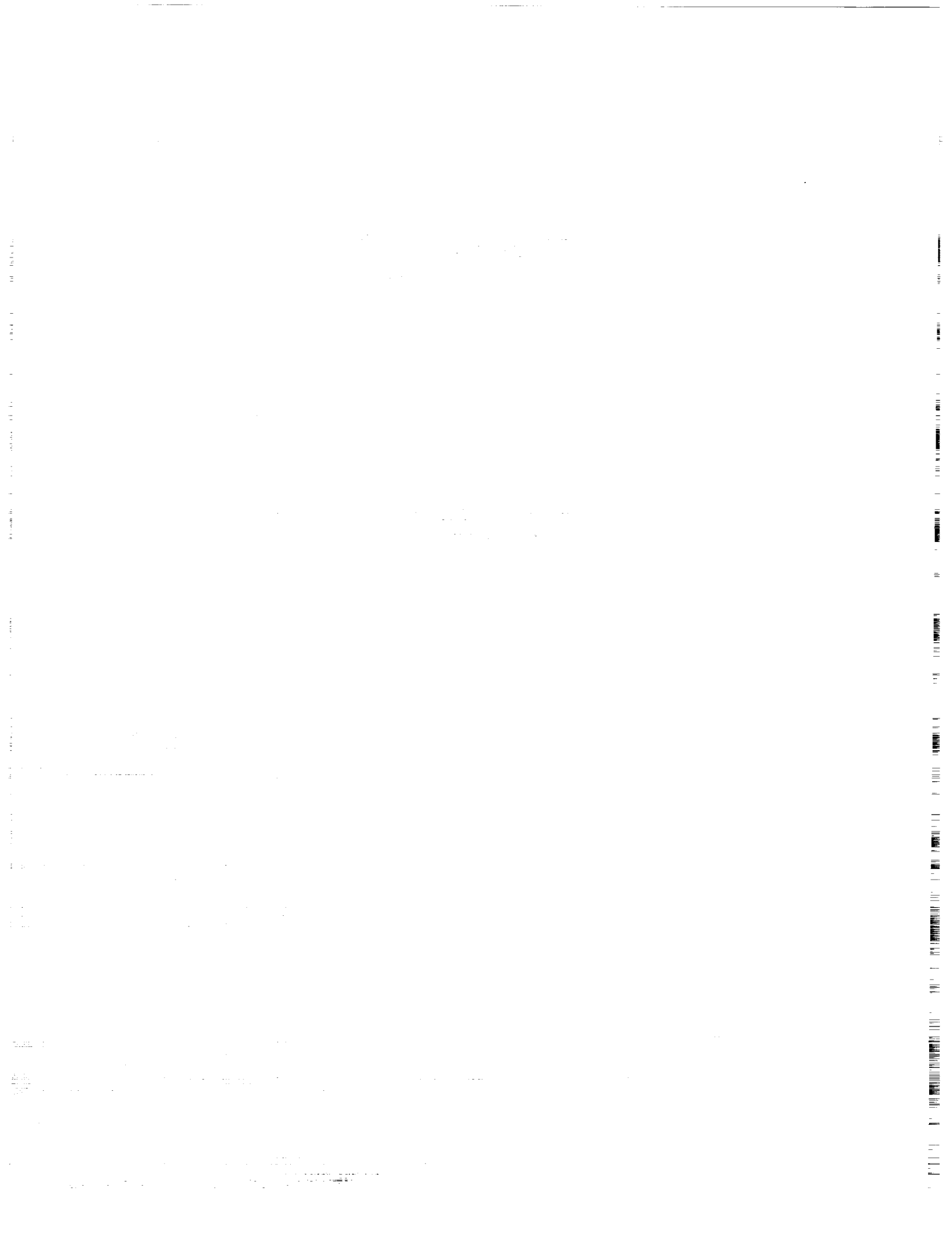
INTRODUCTION

This summary presents a brief view of the substantial progress that has been made (and is continuing to be made) in our understanding of stratospheric transport. The challenge presented by the Atmospheric Effects of Stratospheric Aircraft (AESA) program requires, among other things, further improvement in our modeling ability. The developments outlined below promise to lead to such improvements in the near future. The emphasis here is on conceptual progress, rather than on improvements in modeling per se, as the former has been greater and, to a large degree, is a prerequisite for the latter.

POLAR VORTEX DYNAMICS

The most dramatic change in our understanding of stratospheric transport over the past decade has been the recognition of the importance of polar vortex dynamics to wintertime transport processes. Winter maps of stratospheric potential vorticity reveal (McIntyre and Palmer, 1983) a well-defined "main vortex" with a distinct and usually sharp edge, surrounded by a "surf zone" that is apparently well-mixed through the agency of breaking Rossby waves propagating up the vortex edge. The sharpness of the edge and the distinct nature of air inside and outside the vortex are evident in trace species data from individual ER-2 flights (e.g., Anderson et al., 1989), in AASE-II observations of volcanic aerosol (E. Browell, private communication), and in reconstructions of the distributions of long-lived tracers near the vortex edge during the Airborne Antarctic Ozone Expedition (AAOE) and the Airborne Arctic Stratospheric Expedition (AASE) (Schoeberl et al., 1992).

High-resolution numerical simulations of simple models of the polar vortex (Juckes and McIntyre, 1987) show that, even in the presence of vigorous wave breaking on the vortex edge, the air inside the vortex remains isolated from middle latitude air, hence the "containment vessel" analogy (McIntyre, 1990). This viewpoint appears to be supported by the observed strong gradients at the edge, on two grounds: first, it is difficult to see how sharp gradients of tracers could be maintained in the presence of rapid exchange of air across the edge; second, the strong gradient in potential vorticity represents a strong dynamical restoring force that would tend to inhibit such exchange. Nevertheless, there clearly is, at times, strong transport out of (e.g., Tuck 1992) but not necessarily into the vortex, during a wave-breaking event. (Most of the material transported outward during a breaking event is likely ejected from the outer regions of the vortex, although during a large event, most spectacularly a major warming, inner vortex air may be ejected.) The vortex isolation is, to a large degree, a consequence of the one-sidedness of the wave breaking, a phenomenon that appears to depend on subtle characteristics of the flow structure around the vortex (Juckes and McIntyre, 1987; Polvani and Plumb, 1992). To the extent that wave breaking is indeed confined to the "surf zone," this implies that the induced zonal-mean descent that maintains the polar regions above radiative equilibrium temperatures should, in steady state, be mostly concentrated at the vortex edge (Schoeberl et al., 1992).

Despite these factors, there is observational evidence of a strong depression of tracer mixing-ratio isopleths in the winter polar regions which, among other things, has led to a contrary view of the polar vortex as a "flow processor" (e.g., Proffitt et al., 1990), with substantial exchange of air affecting the interior air mass. At first sight, it seems difficult to reconcile the two views of vortex kinematics. Recent developments do appear, however, to be leading to clarification. The sharp edge gradients of tracers noted above indicate a substantial, but not necessarily total, degree of isolation. Some of the polar depression of tracer isopleths observed in winter is apparently present all year, as suggested by observations in summer (Vedder et al., 1981) and early fall (from high-latitude observations taken during AASE-II in September 1991). Further depression of these isopleths as the vortex is forming during the onset of winter is expected on dynamical grounds, since radiative cooling of the polar regions induces a broad polar descent.

The question is, how much descent is sustained through the winter? If the winter vortex is approximately in steady state, there must presumably be some net inflow across potential vorticity contours as diabatic effects oppose the erosion of the vortex through wave breaking. Moreover, during the northern winter of 1991/1992, there were two apparent "intrusion" events in which inward wave-breaking apparently injected small amounts of extravortex air into the vortex. It is not clear how typical such events are in a "normal" winter.

At the present stage, the evidence leaves little doubt that the vortex air is, to a large degree, isolated from its surroundings, though with occasional vigorous outward transport of air and, perhaps, some weaker transport into the vortex. During major disturbances, of course, the vortex may break up completely; if it reforms, there may be substantial entrainment. The important and unresolved issue is the qualitative one of the magnitude of transport into the vortex as each winter progresses and its significance (if any) for vortex chemistry.

A SUBTROPICAL "BARRIER"?

Our ability to describe large-scale transport processes in low latitudes from observations is hindered by the breakdown there of approximations used to determine balanced winds (and hence potential vorticity). There are several theoretical reasons to expect large gradients of potential vorticity somewhere in the tropics, especially at the equatorward edge of the "surf zone," just as there are strong gradients at its poleward edge. These gradients should also form a partial barrier to transport, though perhaps not as effectively as at the vortex edge (McIntyre, 1990).

Evidence for the existence of this barrier from trace species distributions is limited by the relatively few observations in the tropics, but it does seem to be indicated by, e.g., strong subtropical gradients in latitudinal profiles of $NO_y:O_3$ ratios shown by Kawa et al. (1992). More directly, lidar observations of the Pinatubo aerosol during AASE-II revealed a region of strong gradients in the subtropics (E. Browell, private communication). The concept of a tropical "reservoir" has been advanced to explain the observed behavior of volcanic aerosols following the tropical eruptions of Mt. Agung (Dyer and Hicks, 1968) and Mt. Pinatubo (Trepte and Hitchmann, 1992) and is apparently consistent with the behavior of the radioactive debris from the Hardtack series of bomb tests as described by Danielsen et al. (1991). The tropical reservoir is apparently depleted by erosion of tropical air into the winter hemisphere, leading to decay of the reservoir over a few years.

STRATOSPHERE-TROPOSPHERE EXCHANGE AND DOWNWARD INFLUENCE

It is now well established that stratospheric air is injected into the troposphere in tropopause folds in the region of upper tropospheric jets (e.g., Danielsen et al., 1987). This process appears to be a synoptic-scale analog, on the tropopause, of planetary-scale wave breaking at the edge of the polar vortex (Hoskins et al., 1985) and, apparently, is similarly one-sided (to a large degree, at least). There is also evidence from the stratosphere-troposphere exchange project (STEP) observations of folding on smaller scales associated with inertia-gravity waves (Danielsen et al., 1991), including the possibility of some injection of tropospheric air into the middle latitude lower stratosphere (Kritz et al., 1991). Such injection into the lower stratosphere is consistent with the observed location of the hygropause a few kilometers above the tropopause, though the observed dryness of the hygropause region puts limits on the possible extent of upward transport of tropospheric air.

The rate at which stratospheric air enters the middle- and high-latitude troposphere can be estimated by attempting an inventory of the magnitude and frequency of folding events (e.g.,

Follows and Austin, 1992). However, Haynes et al. (1991) have argued that consideration of such details is unnecessary and that the net mass flux through the tropopause must be determined by the large-scale subsidence from the stratosphere, which is driven from above by stratospheric planetary waves. (Holton [1990] has used this approach to estimate the gross exchange rate.) That is not to say that these two processes are causally linked (they are not, for the most part) but, presumably, that the troposphere–stratosphere system can come into climatological equilibrium only when the transfer rate of mass via tropopause folding matches that supplied by lower stratospheric subsidence. Whether this means that transport of stratospheric constituents into the middle-latitude troposphere is entirely controlled by the mean circulation depends, among other things, on the extent to which tropopause folding is truly one-sided (since a two-way exchange could transport trace constituents without net transport of mass). Moreover, the extent to which the net exchange is controlled by stratospheric planetary wave activity depends also on the extent to which these waves control the mean circulation, in the tropics as well as in middle latitudes.

THE TROPICAL STRATOSPHERIC CIRCULATION

Many past efforts in tropical stratospheric dynamics have focused on the semiannual and quasi-biennial oscillations in the region and their dependence on equatorial waves. It is perhaps ironic that less attention seems to have been directed to the mean (seasonal) circulation there. In low latitudes, the angular momentum constraints that determine the meridional circulation become less effective and the circulation becomes less dependent on the presence of waves. It is well recognized (Held and Hou, 1980) that the tropospheric Hadley circulation is thermally driven (and is confined to the tropics for that reason). Dunkerton (1989) showed that a similar, though deeper and broader, circulation exists in a simplified stratospheric model. This circulation is quite different from that of the middle latitude, where wave transport of potential vorticity is the fundamental driving mechanism. In fact, Hou et al. (1991) went so far as to suggest that the southern hemisphere stratospheric circulation is similar to that which would exist in the absence of wave driving. However, this scenario appears inconsistent with the failure of current general circulation models to simulate accurately stratospheric temperatures near the south pole in winter (Mahlman, private communication).

The distinction between wave-driven and thermally driven circulations is important on several grounds. If, as there are reasons to believe, potential vorticity transport is mostly associated with wave breaking, the middle latitude regime of the wave-driven circulation implies a balance between quasi-isentropic mixing and mean advection, implying that these two transport processes are of comparable importance. One implication of this (Plumb and Ko, 1992) is that it is not appropriate, and can be quite misleading, to interpret the mean (Brewer-Dobson) circulation in terms of air parcel motions. (This point has also been made on different grounds, by Danielsen et al. [1991].) The characteristics of transport in thermally-driven, advection-dominant circulation are quite different. A second reason is the sensitivity of transport to changes in radiatively active constituents such as ozone and CO_2. In wave-driven circulation, radiative changes influence the mean circulation only to the extent that the wave characteristics are affected; in a thermally driven (tropical) regime, the mean circulation is directly dependent on such changes. Third, the tropical circulation (depending on its magnitude) may exert a substantial influence on the rate of troposphere–stratosphere exchange. Thus, clarification of the dynamics of the tropical circulation is a major requirement for the near future.

TRACER CORRELATIONS AND WHAT THEY TELL US

It has been observed that species concentration data from, say, balloon- or aircraft-borne instruments, show simple, and frequently linear, correlations between different species. Such

relationships have been exploited to highlight anomalous chemistry, manifested as anomalies in the correlation (e.g., use of the NO_y:N_2O relationship to reveal denitrification [Fahey et al., 1990]). The correlations appear to be most robust when the two species being correlated have very long lifetimes (an extensive presentation of such correlations from data and model output can be found in Kawa et al. [1992]).

An interpretation of these findings was given by Plumb and Ko (1992), following earlier theoretical developments by Mahlman et al. (1986) and Holton (1986). The latter authors argued that the stratospheric distribution of all long-lived tracers is similar in the sense that their mixing-ratio isopleths follow "equilibrium slopes" and are determined by the competing effects of vertical advection and quasi-isentropic diffusion. Plumb and Ko pointed out that this implies that the correlation diagram between any two such species would be compact, rather than scattered. Moreover, the slope of the diagram is simply equal to the ratio of net global, upward fluxes of the two species. If both species are so long-lived that their net upward fluxes are locally constant with height, the correlation diagram becomes locally linear.

Correlation diagrams of this kind have recently found a number of applications. One relies on the relation between correlation slope and species fluxes to give a direct method of determining stratospheric lifetimes from localized stratospheric measurements (Ko et al., 1992). A second application derives from the related fact that, whereas the existence of the simple relationships is a manifestation of transport dominance, the details of the correlation diagram are dependent on chemical sources and sinks. Thus, such diagrams provide a useful basis for comparison of model results with observation, eliminating much of the complexity associated with comparison of, say, latitude-height cross-sections. (A detailed comparison between models and observation is presented by Kawa et al. [1992].)

These results appear to have significant implications for our understanding of stratospheric transport. On theoretical grounds, the existence of compact correlations depends on quasi-isentropic, diffusion-like transport being more rapid than advection by the meridional circulation. As noted above, this implies that one cannot conceptualize stratospheric transport on climatological time-scales in terms of the motion of air parcels in a Brewer-Dobson circulation; individual air parcels are torn apart long before they can be advected over significant distances. The role of advection under these circumstances is to modify the nature of the "diffusion," particularly in altering the directions of net diffusion. Among other things, this implies that the rate of downward transport of pollutants from a lower stratospheric injection is sensitive to the rate of horizontal mixing.

One common feature of correlation diagrams from models, which is also suggested from whatever observed data there are, is that the correlations seem to be less compact in the tropics than elsewhere. This feature could simply indicate more rapid photochemistry there, or it could indicate that the characteristics of tropical transport are different from those of midlatitudes. This again points to a need for better understanding of dynamics and transport in the tropical stratosphere.

FUTURE DIRECTIONS

Although there are special areas of relevance to the AESA program (such as the rate of stratosphere-to-troposphere exchange), successful transport modeling for this question will require further progress over the broad range of stratospheric transport issues. Some of the most obvious needs are the following:

- Transport in the tropics. What are the main dynamical balances in the seasonal circulation? How important is wave transport in driving the mean circulation and in

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transporting tracers? How effective is the subtropical "barrier" and does it separate two distinct transport regimes?

- Cross-tropopause transport. How much transport is upward and how deep does such transport extend? What is the latitudinal and seasonal variation of cross-tropopause exchange? How well is this modeled and how can it be modeled better?

- Polar vortex transport. How much transport extends into the vortices in winter and is it significant? What is the fate of pollutants emitted directly into the Arctic vortex?

- Role of synoptic-scale eddies in the lower stratosphere. Do synoptic scale-motions behave the same way as planetary waves? How do they affect transport across the edge of the polar vortex? Do we need to care about the synoptic-scale details of cross-tropopause transport?

- What is the intensity of summertime transport, especially in the lower stratosphere? What will be the fate of pollutants emitted into the summer lower stratosphere?

- What can tracer correlations tell us about the nature of transport, especially near the tropopause?

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Chapter 5

Ozone Response to Aircraft Emissions: Sensitivity to Heterogeneous Reactions

Malcolm K. W. Ko and Debra K. Weisenstein
Atmospheric and Environmental Research, Inc.
Cambridge, MA
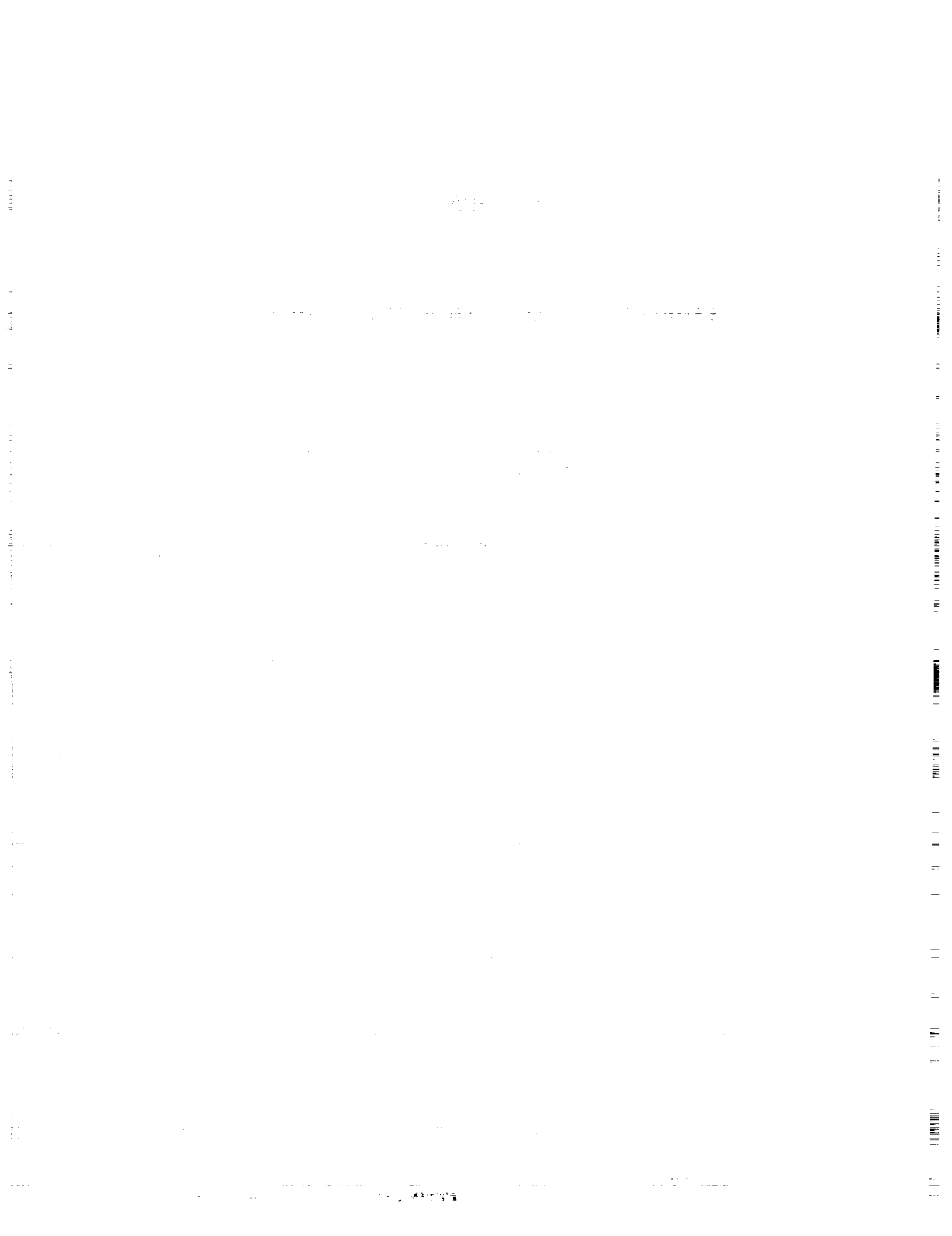
INTRODUCTION

As indicated in the first annual report (Prather et al., 1992), these model calculations should be viewed more as sensitivity studies, primarily designed to:

- Allow for intercomparison of model predictions

- Focus on the range of fleet operations and engine specifications giving minimal environmental impact

- Provide the basis for future assessment studies.

The basic scenarios were chosen to be as realistic as possible using available information on anticipated technology. They are not to be interpreted as a commitment or goal for environmental acceptability.

EMISSION SCENARIOS FOR SUPERSONIC AND SUBSONIC AIRCRAFT

For two-dimensional models that simulate the zonal-mean (averaged over longitude) distributions of the trace gases, one must specify the distributions of the emitted materials as functions of latitude, height, and season. The reader is referred to Chapter 5 in Prather et al. (1992) for details. A brief summary is given here.

The calculations are performed for supersonic fleets with cruise fuel use of 70×10^9 kg/year. This value corresponds to a realistic, economically feasible HSCT fleet of approximately 500 aircraft. Fuel use during takeoff, climb, and descent will be ignored in these calculations. Fuel use and emissions are assumed to be uniform throughout the year.

The adopted latitudinal distribution of fuel use is given in Table 1. The fuel use is distributed according to projected flight paths along which the emitted materials are assumed to be deposited. No adjustment is made to account for the vertical and meridional transport of the plume that may occur in the first few weeks before the emitted material becomes zonally mixed. Also given in Table 1 are the cruise altitudes and emission indices.

The model-calculated ozone responses are examined in terms of the changes relative to the baseline atmosphere circa 2015 (see Table 2 in Chapter 5, Prather et al. [1992]) containing a subsonic fleet. The impact of the subsonic fleet is represented by emissions at two cruise altitudes, 20,000-30,000 ft and 30,000-40,000 ft, with an assumed fuel use of 20×10^9 kg/year and 150×10^9 kg/year, respectively.

This update focuses on the effect of heterogeneous reactions on the expected ozone response. We will concentrate on the results from scenarios A, F, and G, which represent three cases with NO_x EI=15 and cruise speeds of Mach 2.4, 3.2, and 1.6, respectively. Additional results from scenarios B, C, and D (representing the same set of cruise speeds with NO_x EI=5) and from scenario E (representing a fleet with NO_x EI=45 flying at Mach 2.4) will be provided where available.

THE PARTICIPANTS

The modeling groups that participated in the intercomparison are:

AER: Atmospheric and Environmental Research Inc., M. Ko and D. Weisenstein

DuPont: D. Fisher, R. Nopper, and C. Hales

GSFC: NASA Goddard Space Flight Center, C. Jackman and A. Douglass

Italy: G. Pitari, G. Visconti, and E. Mancini

LLNL: Lawrence Livermore National Laboratory, D. Wuebbles and D. Kinnison

MPI: Max Planck Institut für Chemie, C. Bruhl

NCAR: National Center for Atmospheric Research, G. Brasseur, X. Tie, C. Granier, and I. Folkins

The modeling groups were asked to provide results from both gas-phase-only calculations (case I) and gas-phase reactions plus heterogeneous reactions (case II). Four of the modeling groups (AER, GSFC, LLNL, and NCAR) provided model results for the previous report. Three of the four (AER, GSFC, and NCAR) have modified their models over the past year; the gas-phase-only results differ slightly from those reported in Prather et al. (1992). The LLNL results for case I are identical to results from last year.

The procedure for this intercomparison assessment made use of the Upper Atmosphere Data Program (UADP) facilities at NASA Langley. Model results in a standard grid and format were compiled in the UADP database. Each modeling group was asked to send at least 4 months (March 15, June 15, September 15 and December 15) of latitude-height fields of NO_y, H_2O, Cl_y, O_3, and noon-time $NO + NO_2$ (NO_x); and latitude-season (12 months) of the column abundance of O_3 for each simulation.

DESCRIPTION OF HETEROGENEOUS CHEMISTRY

It has been noted (WMO, 1990) that the ozone decrease over the past decade predicted by models using gas-phase chemistry is smaller than the observed trend. A most likely explanation is the omission of the effect associated with enhanced concentrations of the active chlorine species produced by heterogeneous reactions occurring on the polar stratospheric cloud and the global aerosol layer (Hoffman and Solomon, 1989; Brasseur et al., 1990; Rodriguez et al.,1991; Pitari et al., 1991). Laboratory studies indicate that two of the heterogeneous reactions proceed at appreciable rates on sulfuric acid solution at stratospheric temperatures. These are

$$N_2O_5 + H_2O \;\rightarrow\; 2HNO_3 \tag{1}$$

and

$$ClNO_3 + H_2O \;\rightarrow\; HNO_3 + HOCl \tag{2}$$

Inclusion of these two reactions brings models into closer agreement with the observed ozone trend at middle latitudes, though differences in latitudinal and seasonal gradients still exist.

In the calculations, heterogeneous conversion of N_2O_5 and $ClONO_2$ on the aerosol layer is parameterized as the product of the collision frequency of the molecule with the aerosol particles (ν) and the reaction probability per collision (γ). The parameterization follows the prescription in chapter 8 of WMO (1992). The collision frequency is defined to be

$$\nu = 5200 \ (cm/s) \times \text{surface area per unit volume} \ (/cm)$$

where the surface area is given in Table 2, and the effective collision velocity of 5200 cm/s is for a species with gm molecular weight of 100 at typical stratospheric temperature.

The reaction probability and products for the two reactions are given in Table 3. The temperature dependence given for the $ClONO_2$ reaction simulates the dependence on the water content of the aerosol. The formula was obtained by fitting the laboratory data of Tolbert et al. (1988). In both cases, it is assumed that the products are immediately emitted to the atmosphere in the gas phase.

Though the rates for reactions (1) and (2) have been measured in the laboratory under simulated atmospheric conditions, it is unclear whether differences in the nature of the particulate surfaces would make any quantitative difference in the rates. Attempts to use observed concentrations of ClO and NO at middle latitudes to determine whether there is evidence for the reactions have been inconclusive (see e.g., Rodriguez et al., 1991; King et al., 1991; Considine et al., 1992). In addition, the existence of other reactions that may occur on sulfate aerosols and alter the response of ozone cannot be ruled out. We also do not address the effects of other heterogeneous reactions that could occur on PSCs and the possibility of enhanced PSC formation that could occur in the aircraft contrail due to emissions of H_2O and HNO_3 (Peter et al., 1991). Increase in PSC could cause additional O_3 decrease by converting more chlorine reservior species to active chlorine species. This O_3 decrease could be counted as an indirect effect of the aircraft emissions.

MODEL RESULTS

Background Atmosphere

The effect of the two heterogeneous reactions is to convert NO_x to HNO_3. Rodriguez et al. (1991) argued that, at the background surface area, reaction (1) is more effective than reaction (2). The effect is largest at high-latitude winter where the N_2O_5/NO_y ratio is larger because of the lack of sunlight. Figures 1a and 1b show the calculated $(NO + NO_2)/NO_y$ ratio for the background atmosphere from the different models for case I (Figure 1[a], the gas phase only) and case II (Figure 1[b], gas phase + heterogeneous reactions). Results from the figures indicate that the impact is largest poleward of 30° in the lower stratosphere.

In the previous model intercomparison, it was reported that the column abundances of O_3 calculated by the different models using gas-phase chemistry for the 2015 atmosphere are within 20% of each other. The inclusion of the two heterogeneous reactions maintained the same agreement. In the work of Weisenstein et al. (1991) there were indications that heterogeneous reactions reduce the efficiency of the NO_x cycle but enhance the efficiency of the ClO_x and HO_x cycle to compensate for the ozone removal rate. As a result, the column abundances calculated with and without heterogeneous chemistry are quite similar for each model. This is illustrated in Figures 2(a) and 2(b).

In spite of the large differences in the calculated $NO + NO_2$ among the models, the calculated O_3 columns all contain the same basic features. This suggests that there may be significant

differences in the functional dependence of O_3 on the calculated photochemical removal rates in the different models. For instance, it is likely that the transport parameters are quite different among the models.

Change in NO_y

The inclusion of heterogeneous chemistry is not expected to affect the calculated change in NO_y in any significant way. All models showed different residence times for different injection heights. The model-calculated changes in NO_y for scenarios A, F, and G are shown in Figures 3-5, respectively. Only results from case II are shown because the corresponding results from case I are almost identical. For scenario F (Mach 3.2 and EI=15), all models showed an increase of more than 1 ppbv extending all the way to the southern hemisphere. Except for the NCAR model, the calculated increase in an extended region corresponding to the flight region is over 4 ppbv. For scenario A (Mach 2.4 and EI=15), the increase in the southern hemisphere is about 0.5 ppbv, with the maximum local increase in the northern latitudes ranging from 1 to 4 ppbv. For scenario G (Mach 1.6, EI=15), most models show an increase in the southern hemisphere of about 0.1 to 0.2 ppbv with the maximum in the northern latitudes of about 0.4 ppbv.

Ozone Response

In contrast to the case with chlorine increases, including heterogeneous reactions in the HSCT model calculations will actually give smaller ozone decreases due to NO_x increases (Weisenstein et al., 1991). The altered response of ozone to NO_x injection with heterogeneous chemistry included can be explained by changes in the relative magnitudes of the catalytic cycles, which remove ozone. These cycles involve NO_x, Cl_x, HO_x, O_x, and Br_x radical species. The NO_x cycle accounts for more than half of the ozone loss in both winter and summer with gas-phase chemistry only. The effect of the heterogeneous reactions $N_2O_5 + H_2O \rightarrow 2HNO_3$ and $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ is to repartition the odd-nitrogen family, resulting in NO_x concentrations that are reduced by 80% in winter and 40% in summer between 10 and 20 km at midddle and high latitudes as compared with gas-phase-only calculations. Thus, the ozone loss due to the NO_x cycle becomes a much smaller fraction of the total ozone loss. Increases in OH and ClO due to inclusion of the heterogeneous reaction cause the contributions from the HO_x and Cl_x cycles to nearly double, compensating for much of the decrease in the NO_x cycle.

Addition of nitrogen oxides from HSCT emissions results in a 20-30% increase in the NO_x cycle with or without the heterogeneous reactions. However, the ozone response is much less sensitive to the NO_x increase with heterogeneous chemistry included because of the reduced role of NO_x in regulating total ozone loss. Furthermore, an increase in the NO_x concentration will enhance the concentration of $ClONO_2$, HNO_3, and HO_2NO_2 and thus reduce the Cl_x and HO_x catalytic destruction of ozone. Depending on the background levels of Cl_x and HO_x and the overall rate of the heterogeneous reactions, HSCT emissions can result in ozone increases.

The calculated changes in column ozone from the scenarios are shown in Figures 6-8. The calculated changes in global ozone content are summarized in Tables 4 and 5 for case II and case I, respectively. The calculated changes at 40°N to 50°N are given in Tables 6 and 7. The percent change in local O_3 from scenarios A, F, and G for March are shown in Figures 9-11.

The following observations can be made about the results:

- For both cases I and II, the results within each individual model show that the calculated O_3 decreases are greater for larger EI and higher cruise altitudes.

- With inclusion of heterogeneous chemistry, the calculated ozone decreases are significantly smaller.

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- All models showed the largest local decreases in the region north of 30°N between 10 and 25 km where most of the NO_x emissions are deposited.

- The results provided indicate that the calculated ozone response may not scale strictly with EI's for the same cruise altitudes. A likely explanation for this is the close balance between the enhanced ozone removal rate in the lower stratosphere and the enhanced O_3 production in the upper troposphere.

- For the cases where the calculated decrease in column abundance of ozone is larger than 1%, the spread among the models in case II is up to a factor of 3.

- The large spread in the model results in case II is due to very different responses in the high-latitude upper troposphere.

CONCLUDING REMARKS

For both cases I and II, the results within each individual model all show similar dependence on EI for NO_x and cruise altitudes. Thus, all the calculated impacts on O_3 are greater for larger EI and higher cruise altitudes. However, the results for the same cruise altitude do not scale strictly with EI. The magnitudes of the calculated O_3 changes among the models differ by as much as a factor of 3. The analysis presented in Prather et al., chap. 5 (1992) suggested that the differences can be understood in terms of the residence time for the injected NO_y and the O_3 response sensitivity factor peculiar to each model. The same still holds and one must continue to look for observations that can help define these quantities.

ACKNOWLEDGMENTS

Table 1. Parameters for Aircraft Scenarios

	Subsonic Cruise short range	Subsonic Cruise long range	Supersonic Cruise
FUEL USE (10^9kg/year)	20	150	all cases 70
CRUISE ALTITUDE (thousand feet [km])	20-30 (6.1-9.1)	30-40 (9.1-12.2)	Mach 1.6 : 47-57 (14.3-17.4) Mach 2.4 : 55-65 (16.8-19.8) Mach 3.2 : 70-80 (21.3-24.4)

LATITUDINAL DISTRIBUTION OF FUEL USE (percent)
(long range and short range)

80°N-90°N	0.	.6
70°N-80°N	.4	.7
60°N-70°N	2.9	.7
50°N-60°N	15.7	12.3
40°N-50°N	25.2	28.4
30°N-40°N	31.6	18.4
20N-30°N	11.0	8.4
10°N-20°N	3.7	6.7
Eq-10°N	2.4	6.3
Eq-10°S	1.7	4.9
10°S-20°S	1.6	4.2
20°S-30°S	1.6	4.0
30°S-40°S	2.0	3.1
40°S-40°S	.2	1.3
50°S-90°S	0.	0.

EMISSION INDICES (gm/kg fuel)

species	(long range and short range)	
NO_x	20.7	as specified
H_2O	1230	1230
CO	1.1	1.5 (1.2-3.0)
HC (as CH_4)	0.2	0.2 (0.02-0.5)
SO_2	1.1	1.0
CO_2	3160	3160

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Table 2. Recommended Aerosol Surface Areas for Heterogeneous Reactions

	Aerosol Surface Area (10^{-8} cm^2 cm^{-3})									
	Jan - Feb - Mar - Apr - May - Jun					Jul - Aug - Sep - Oct - Nov - Dec				
Z* km	60-90N	30-60N	30N-30S	30-60S	60-90S	60-90N	30-60N	30N-30S	30-60S	60-90S
32	0.03†	0.03	0.10	0.05	0.03	0.25	0.03	0.10	0.08	0.03
30	0.05	0.08	0.18	0.10	0.05	0.05	0.08	0.18	0.15	0.05
28	0.13	0.18	0.33	0.20	0.13	0.13	0.18	0.33	0.25	0.13
26	0.25	0.25	0.43	0.30	0.25	0.25	0.25	0.43	0.38	0.25
24	0.35	0.38	0.50	0.43	0.35	0.35	0.38	0.50	0.50	0.35
22	0.45	0.50	0.63	0.63	0.50	0.45	0.50	0.63	0.63	0.50
20	0.63	0.63	0.75	0.80	0.75	0.63	0.63	0.75	0.75	0.63
18	0.75	0.75	0.75	1.00	1.00	0.75	0.75	0.75	1.00	1.00
16	0.88	0.88	0.50	1.00	1.13	0.75	0.75	0.50	1.00	1.25
14	1.13	1.13	0.50	1.00	1.25	0.88	0.88	0.50	1.25	1.50
12	1.25	1.25	0.50	1.00	1.25	1.00	1.00	0.50	1.25	1.75

Note: Values based on analysis of the SAGE II data by Poole, Thomason and Yue, see Chapter 3, WMO (1992).

Table 3. Reaction Probability (g) for Heterogeneous Conversions

Reaction	γ
(1) N_2O_5 [+ H_2O in aerosol] $\rightarrow$ $2HNO_3$	0.1
(2) $ClONO_2$ [+ H_2O in aerosol] $\rightarrow$ HNO_3 + $HOCl$	$0.006\exp[-0.15*(T-200)]$ *

* T is the local temperature in Kelvin.

Table 4. Percent Change in Global Content, Case II (gas phase + heterogeneous)

	EI = 15				EI = 5		EI= 45
	Mach 3.2 (F)	Mach 2.4 (A)	Mach 1.6 (G)	Mach 3.2 (B)	Mach 2.4 (C)	Mach 1.6 (D)	Mach 2.4 (E)
AER	-1.9	-0.59	0.09	-0.74	-0.28	0.02	-2.4
DuPont	-2.2	-0.69	0.84	-0.67	-0.13	0.41	-4.0
GSFC	-2.4	-0.64	-0.15	-0.80	-0.25	-0.09	-2.6
Italy	-3.2	-0.20	0.51	-1.3	-0.02	0.27	-2.9
LLNL	-1.3	-0.36	0.09				
MPI	-3.5	-0.18	-0.10		-0.05		-1.0
NCAR	-1.3	-0.25	-0.06	-0.19	-0.03	0.	-1.5

Table 5. Percent Change in Global Content, Case I (gas phase only)

	EI = 15				EI = 5		EI= 45
	Mach 3.2 (F)	Mach 2.4 (A)	Mach 1.6 (G)	Mach 3.2 (B)	Mach 2.4 (C)	Mach 1.6 (D)	Mach 2.4 (E)
AER	-5.0	-2.6	-0.44	-1.5	-0.75	-0.10	-8.1
DuPont	-5.7	-3.3	-0.031	-1.7	-0.95	0.09	-9.9
GSFC	-5.4	-2.3	-0.87				
Italy	-6.2	-2.3	-0.12	-2	-0.87	-0.03	-10.1
LLNL	-3.4	-1.7	-0.29	-0.9	-0.50	-0.085	-6.1
MPI	-5.1	-0.56	-0.06				
NCAR	-4.1	-1.7	-0.75				

Table 6. Percent Change in Column, 40-50°N, Case II (gas phase + heterogeneous reaction)

	EI = 15			EI = 5			EI = 45
	Mach 3.2 (F)	Mach 2.4 (A)	Mach 1.6 (G)	Mach 3.2 (B)	Mach 2.4 (C)	Mach 1.6 (D)	Mach 2.4 (E)
AER	-3.3	-0.95	0.09	-1.2	-0.42	0.03	-4.0
DuPont	-3.4	-1.3	0.84	-1.1	-0.31	0.53	-7.4
GSFC	-4.1	-0.63	-0.01	-1.3	-0.23	-0.04	-3.3
Italy	-5.5	-0.42	0.67	-1.9	0.04	0.39	-4.8
LLNL	-2.2	-0.56	0.08				
MPI	-5.0	-0.3	0.1		-0.1		-1.7
NCAR	-2.1	-0.27	-0.03	-0.20	-0.04	0.04	-2.3

Table 7. Percent Change in Column, 40-50°N, Case I (gas phase only)

	EI = 15			EI = 5			EI = 45
	Mach 3.2 (F)	Mach 2.4 (A)	Mach 1.6 (G)	Mach 3.2 (B)	Mach 2.4 (C)	Mach 1.6 (D)	Mach 2.4 (E)
AER	-8.8	-4.6	-0.91	-2.5	-1.3	-0.23	-14.0
DuPont	-8.8	-5.6	-0.77	-2.9	-1.7	-0.12	-16.7
GSFC	-10	-3.7	-1.4				
Italy	-11	-4.1	-0.53	-3.3	-1.47	-0.15	-17.2
LLNL	-5.8	-2.7	-0.5	-1.5	-0.77	-0.14	-9.5
MPI	-7	-1	-0.2				
NCAR	-7.3	-2.9	-1.3				
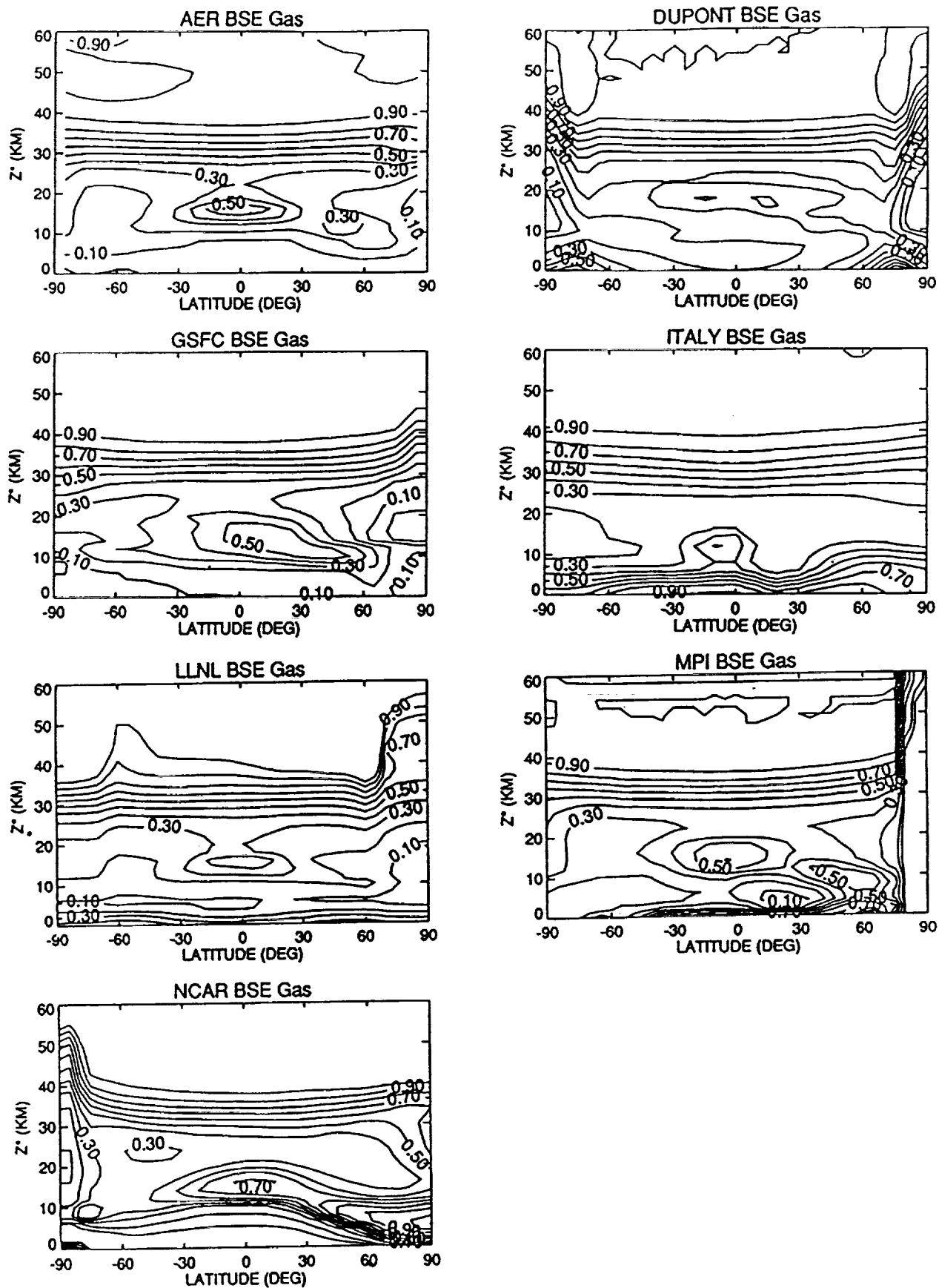
Figure 1a. Calculated latitude-height behavior of $(NO + NO_2)/NO_y$ for March for the baseline (BSE) for the different models for case I, gas-phase reactions only. The contour levels are 0.1 to 1 in steps of 0.1.
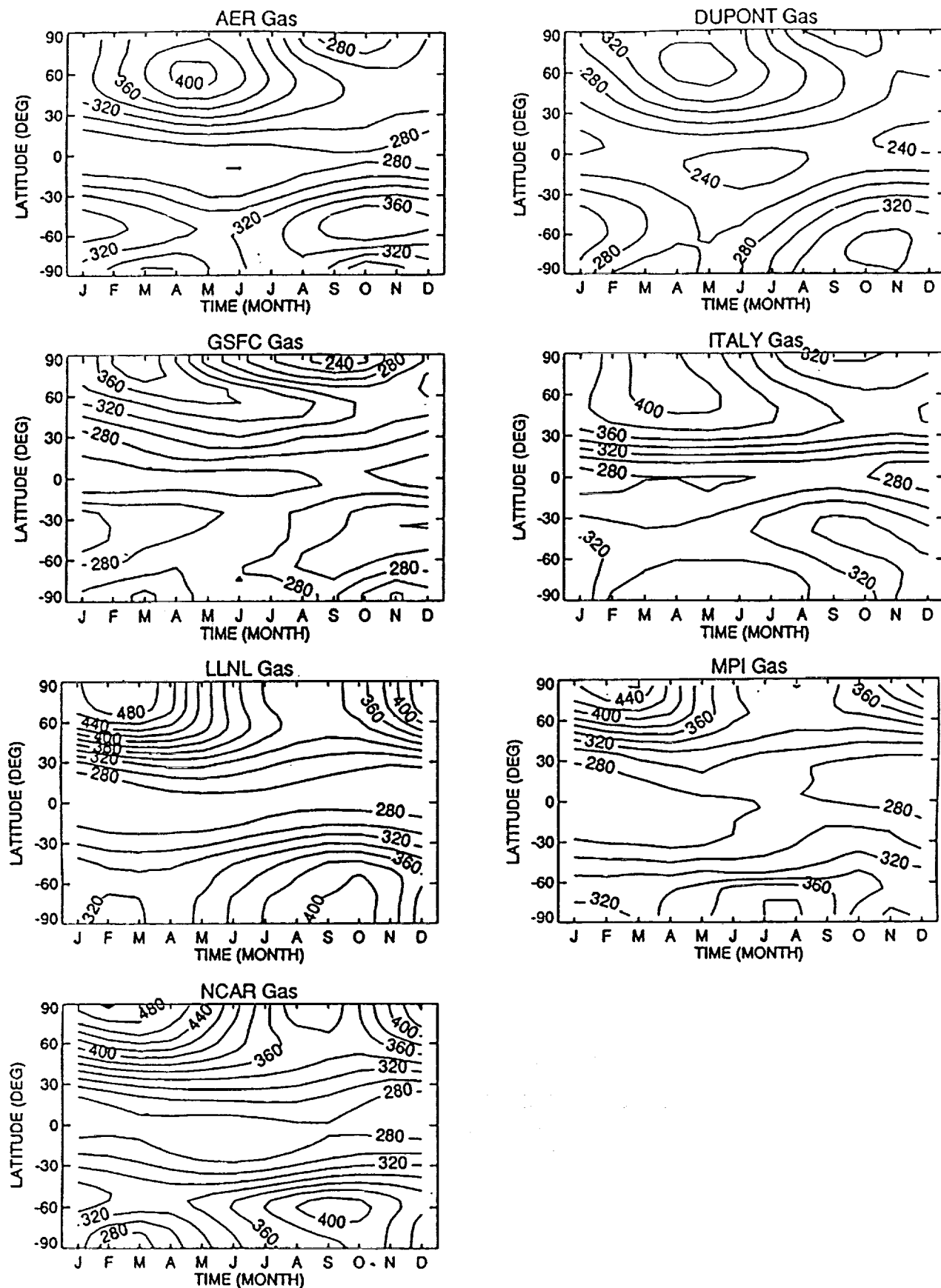
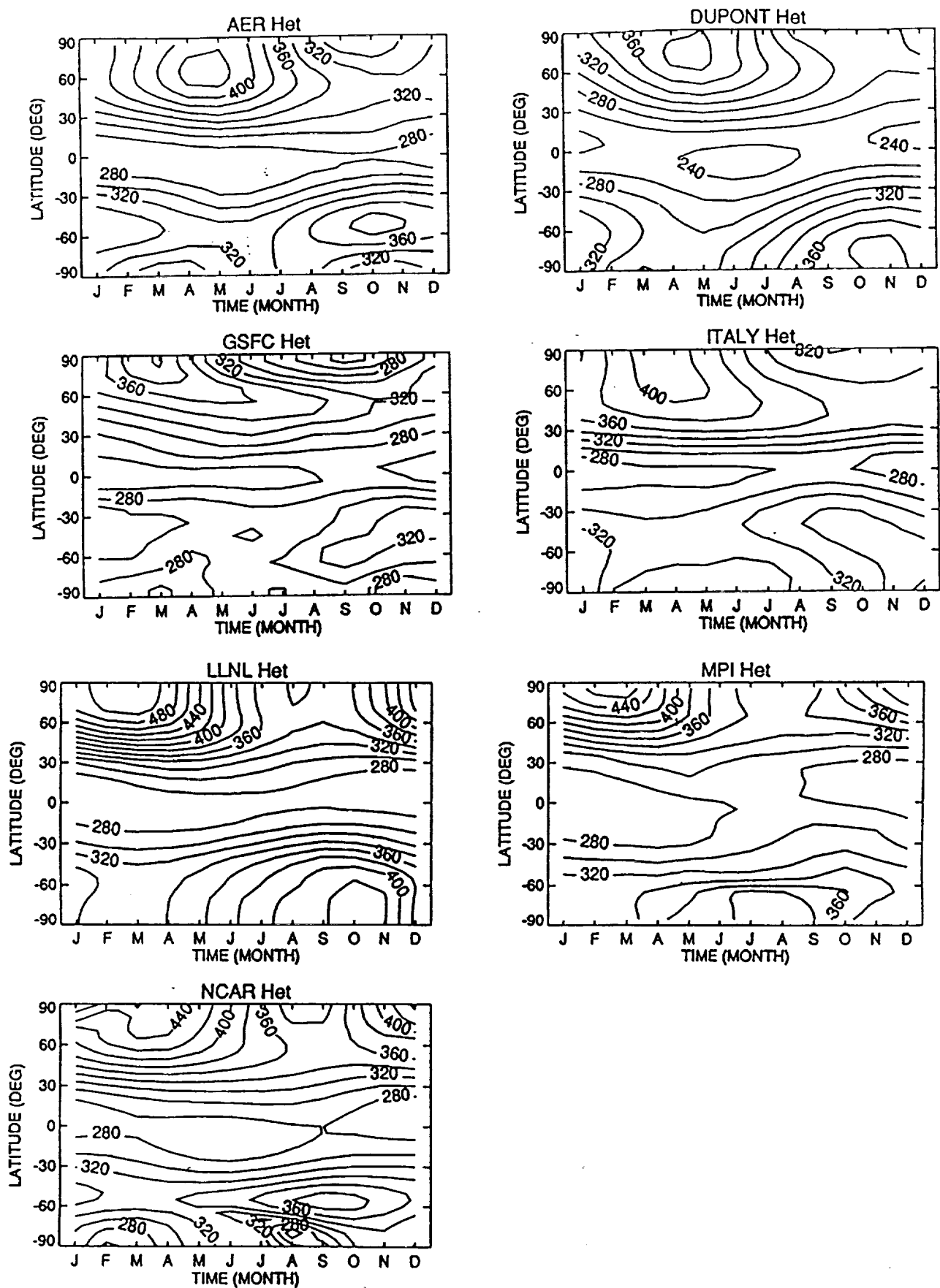94
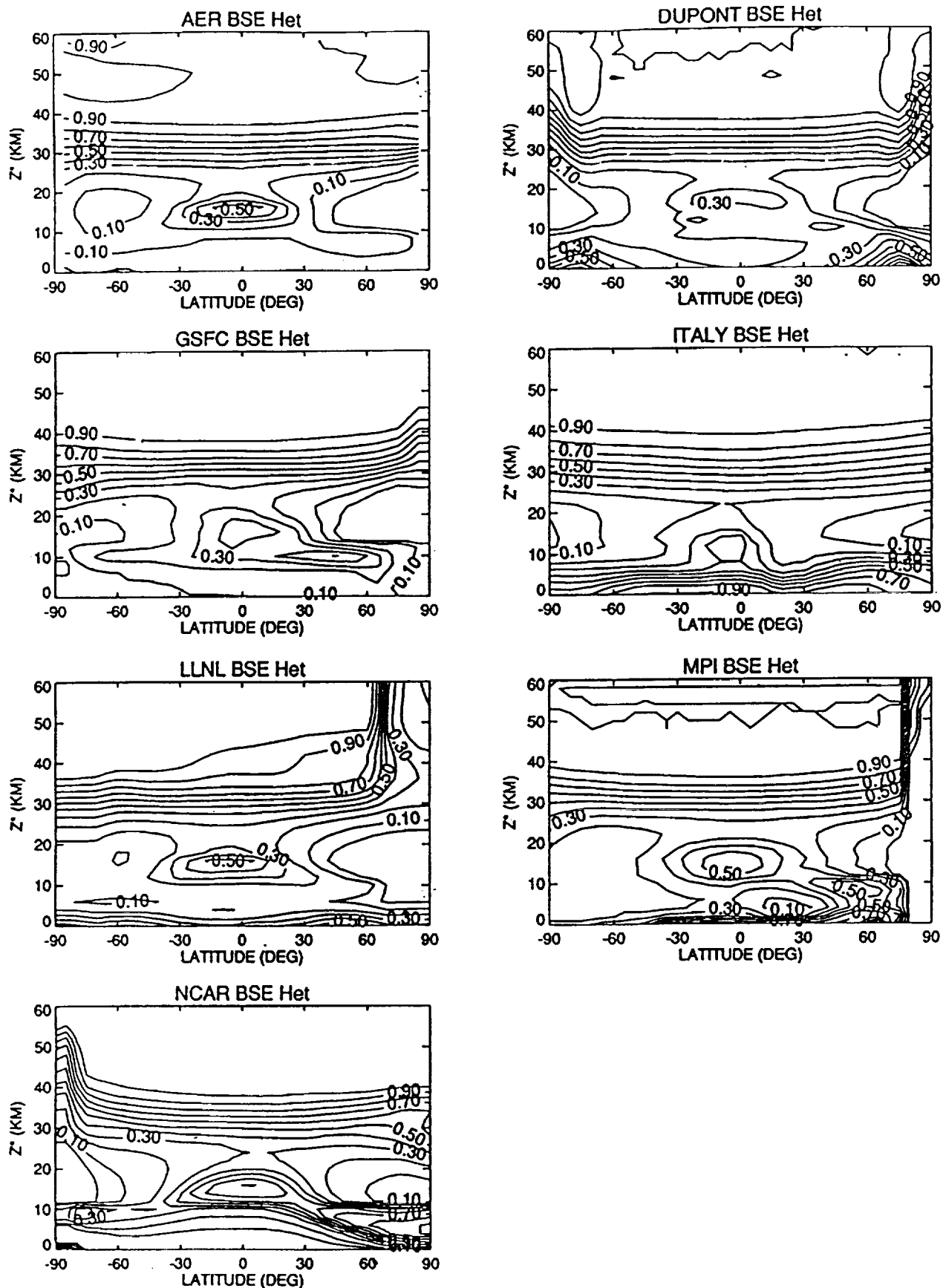
Figure 1b. Calculated latitude-height behavior of $(NO + NO_2)/NO_y$ for March for the baseline (BSE) for the different models for case II, gas-phase reactions + heterogeneous reactions. The contour levels are 0.1 to 1 in steps of 0.1.

Figure 2a. Calculated column abundances of O_3 (Dobson Units) for the baseline (BSE) for the different models for case I, gas-phase reactions only. The contour levels are 240 Dobsons to 500 Dobsons in steps of 20 Dobsons.
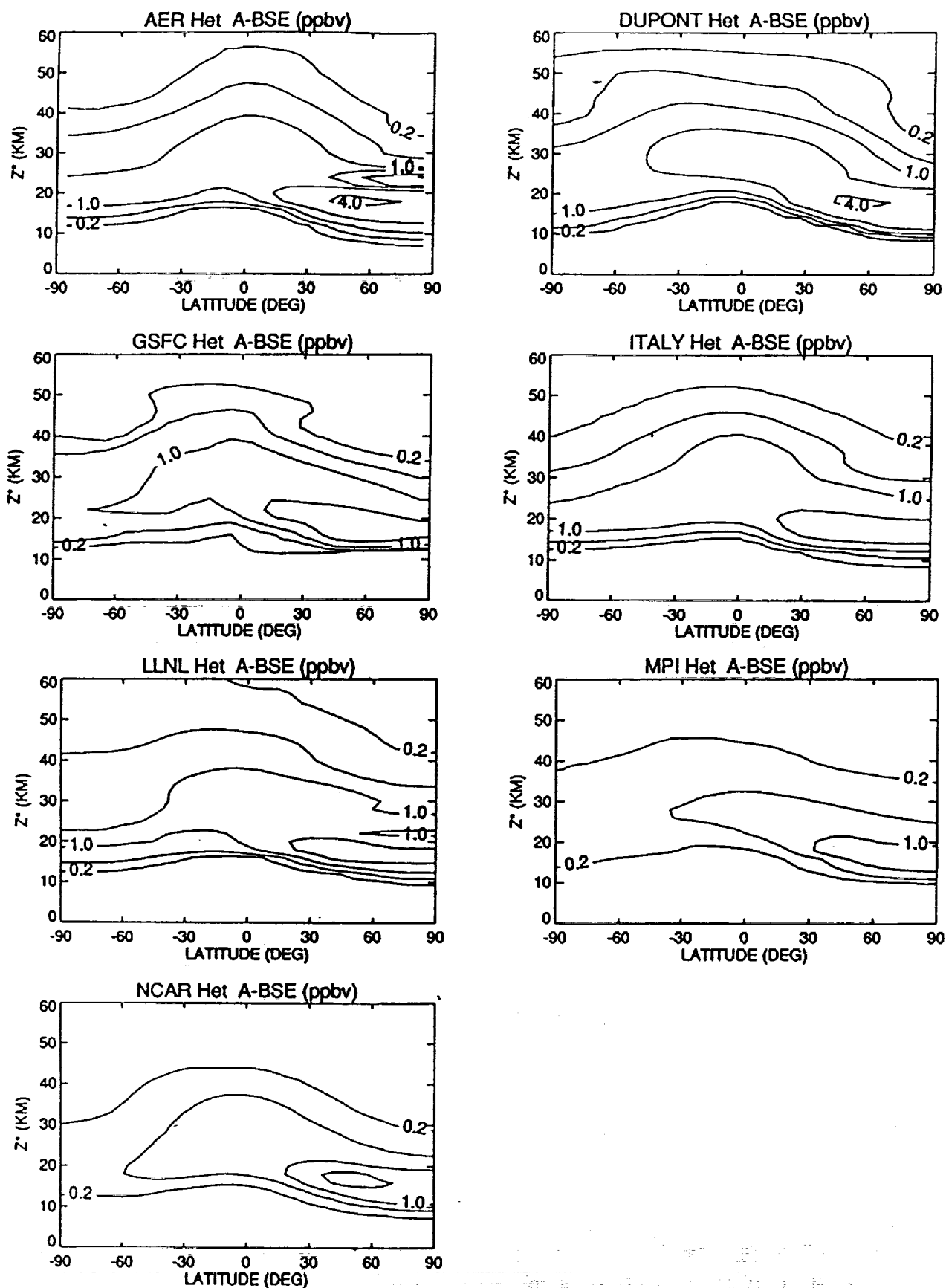
Figure 2b. Calculated column abundances of O_3 (Dobson Units) for the baseline (BSE) for the different models for case I, gas-phase reactions + heterogeneous reactions. The contour levels are 240 Dobsons to 500 Dobsons in steps of 20 Dobsons.
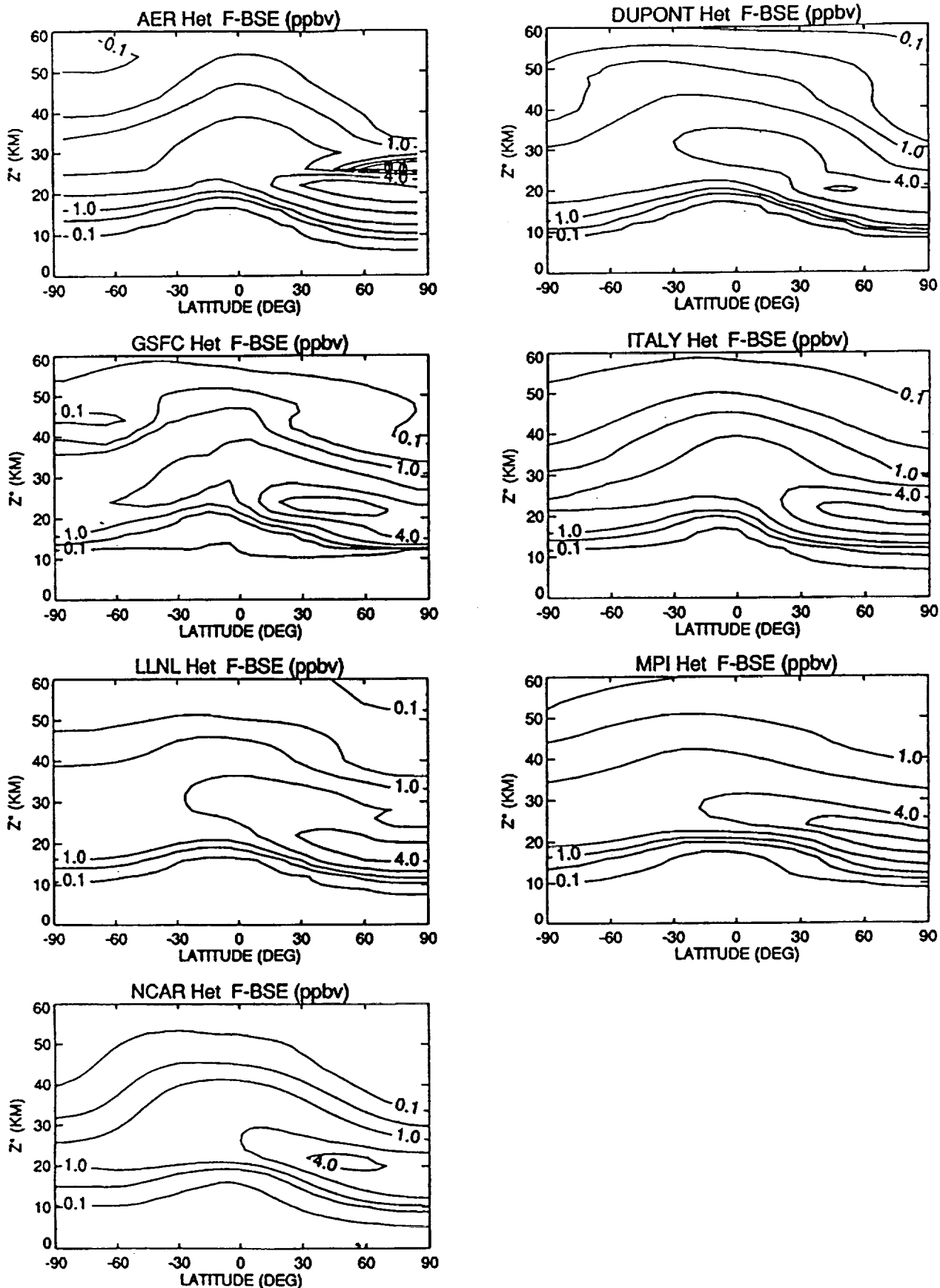
Figure 3. Calculated changes in the concentration of NO_y (ppbv) for March in scenario A relative to the baseline (BSE) for case II. The contours are 0.2, 0.5, 1.0, 2.0, and 4.0 ppbv.

Figure 4. Calculated changes in the concentration of NO$_y$ (ppbv) for March in scenario F relative to the baseline (BSE) for case II. The contours are 0.1, 0.5, 1.0, 2.0, 4.0, and 6.0 ppbv.
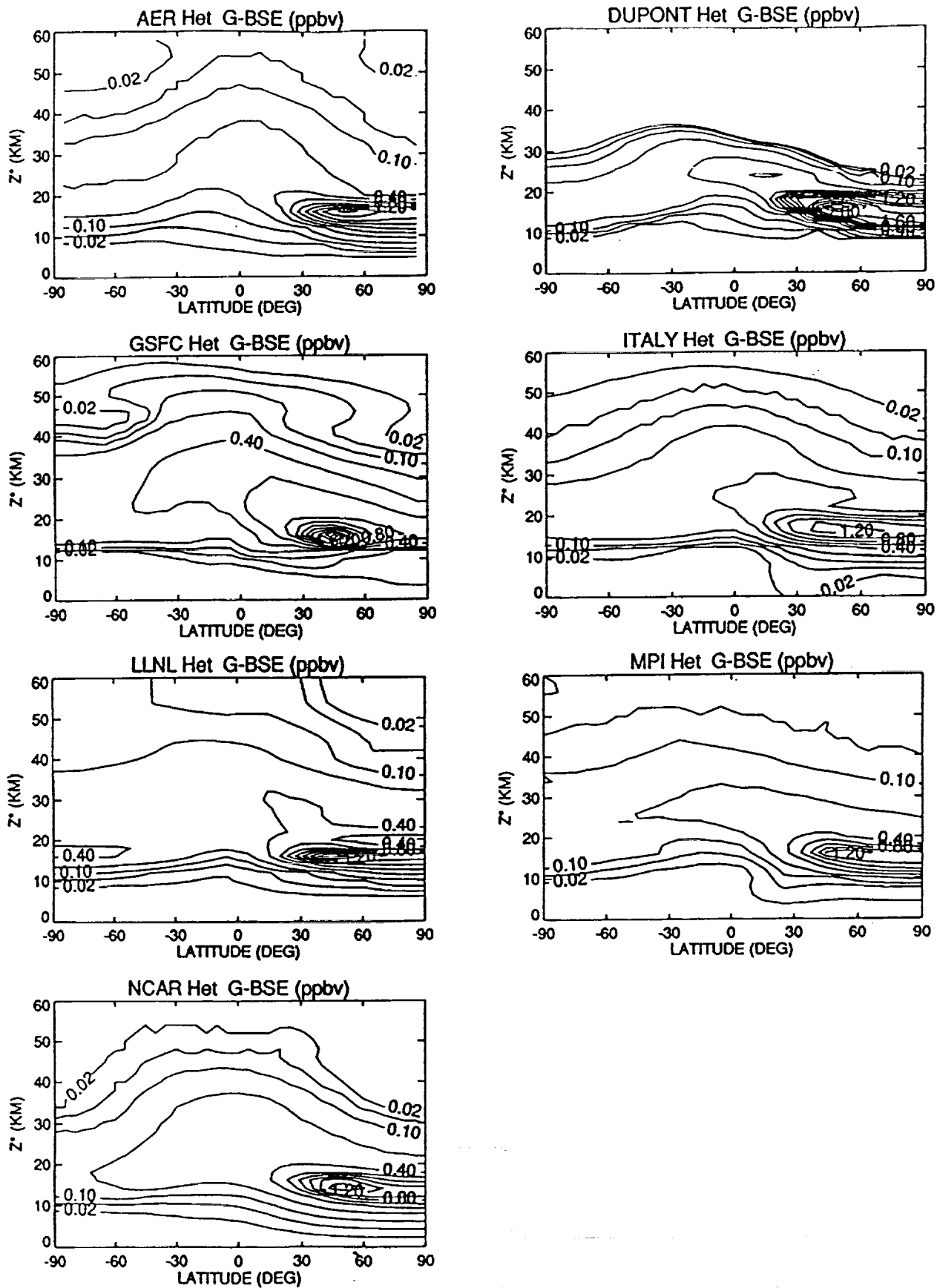
Figure 5. Calculated change in the concentration of NO_y (ppbv) for March in scenario G relative to the baseline (BSE) for case II. The contours are 0.02, 0.05, 0.1, 0.2, and 2.0 in steps of 0.2 ppbv.
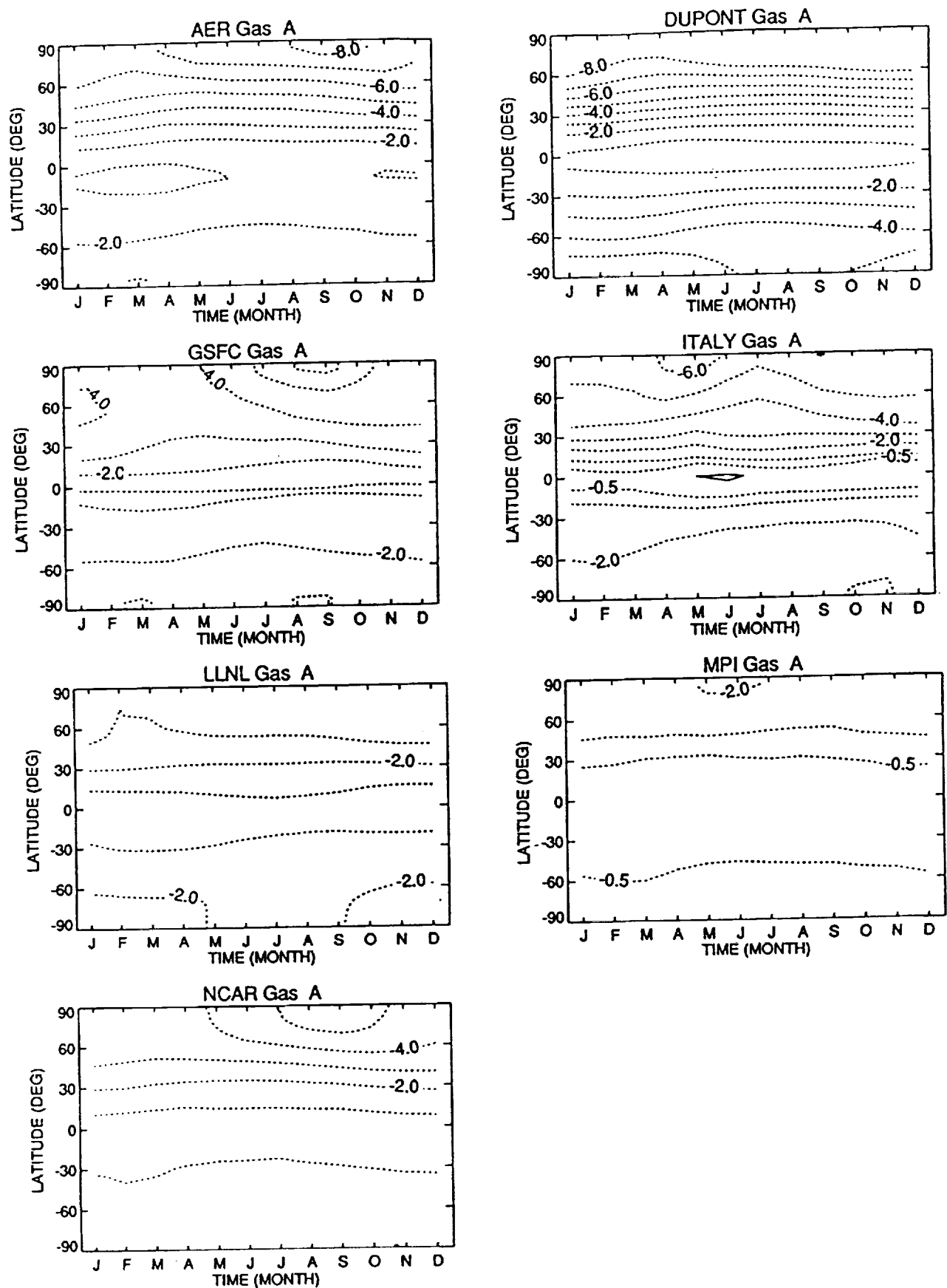
Figure 6a. Calculated percent change in the column abundance of O_3 for the different models as functions of latitude and season in scenario A relative to the baseline (BSE) for case I. The contours are 0, -0.5, and -1.0 to -8.0 in steps of 1%.

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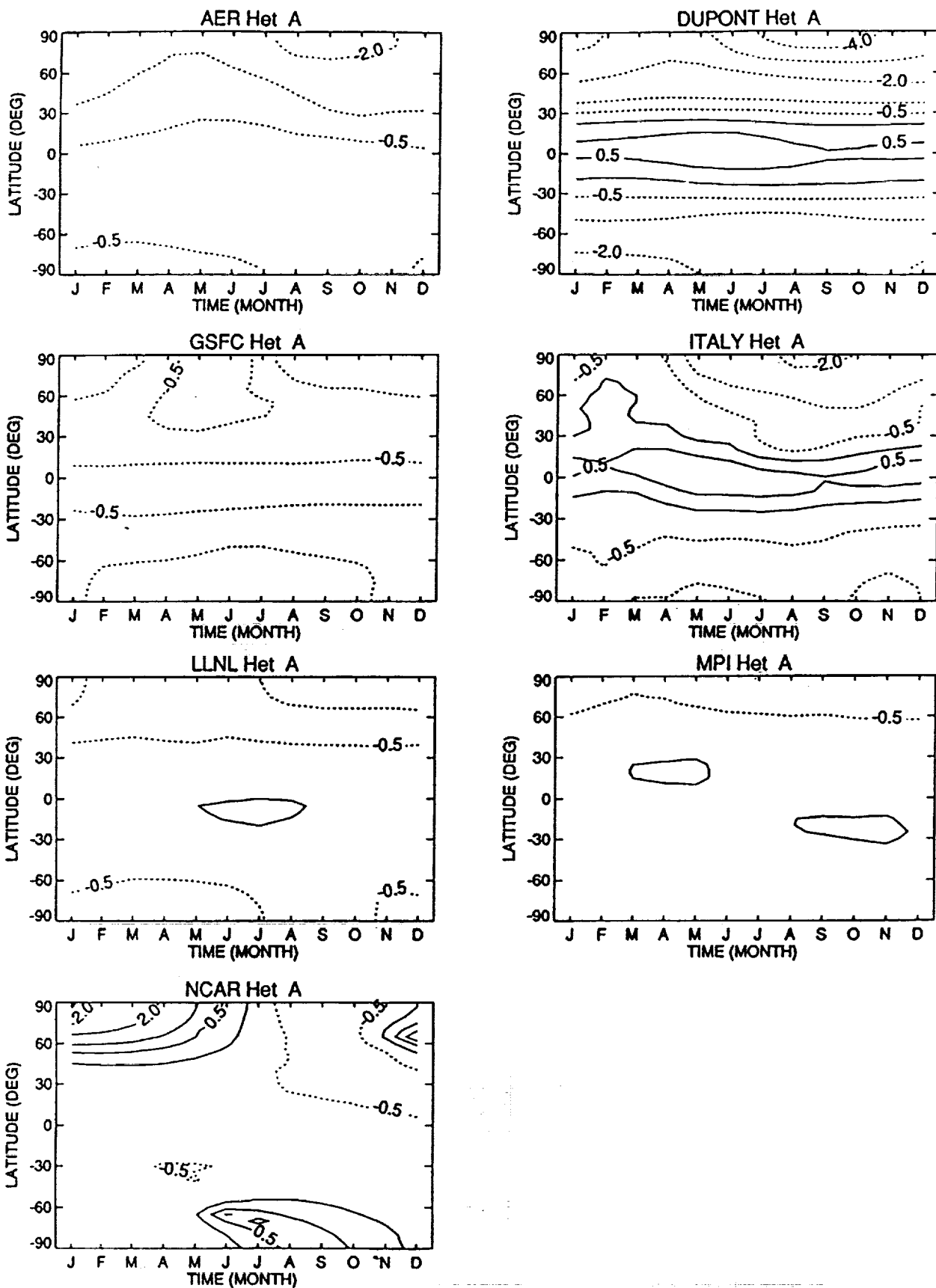
Figure 6b. Calculated percent change in the column abundances of O_3 for the different models as functions of latitude and season in scenario A relative to the baseline (BSE) for case II. The contours are 2, 1, 0.5, 0, -0.5, and -1.0 to -4.0 in steps of 1%.

Figure 7a. Calculated percent change in the column abundances of O_3 for the different models as functions of latitude and season in scenario F relative to the baseline (BSE) for case I. The contours are -16 to -2 in steps of 2.0%.

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Figure 7b. Calculated percent change in the column abundances of O_3 for the different models as functions of latitude and season in scenario F relative to the baseline (BSE) for case II. The contours are +2.0, +1.0, 0, -1.0, and -2 to -8 in steps of 2.0%.

Figure 8a. Calculated percent change in the column abundances of O_3 for the different models as functions of latitude and season in scenario G relative to the baseline (BSE) for case I. The contours are 0.1, 0., -0.1, and -0.2 to -2.0 in steps of 0.2%.
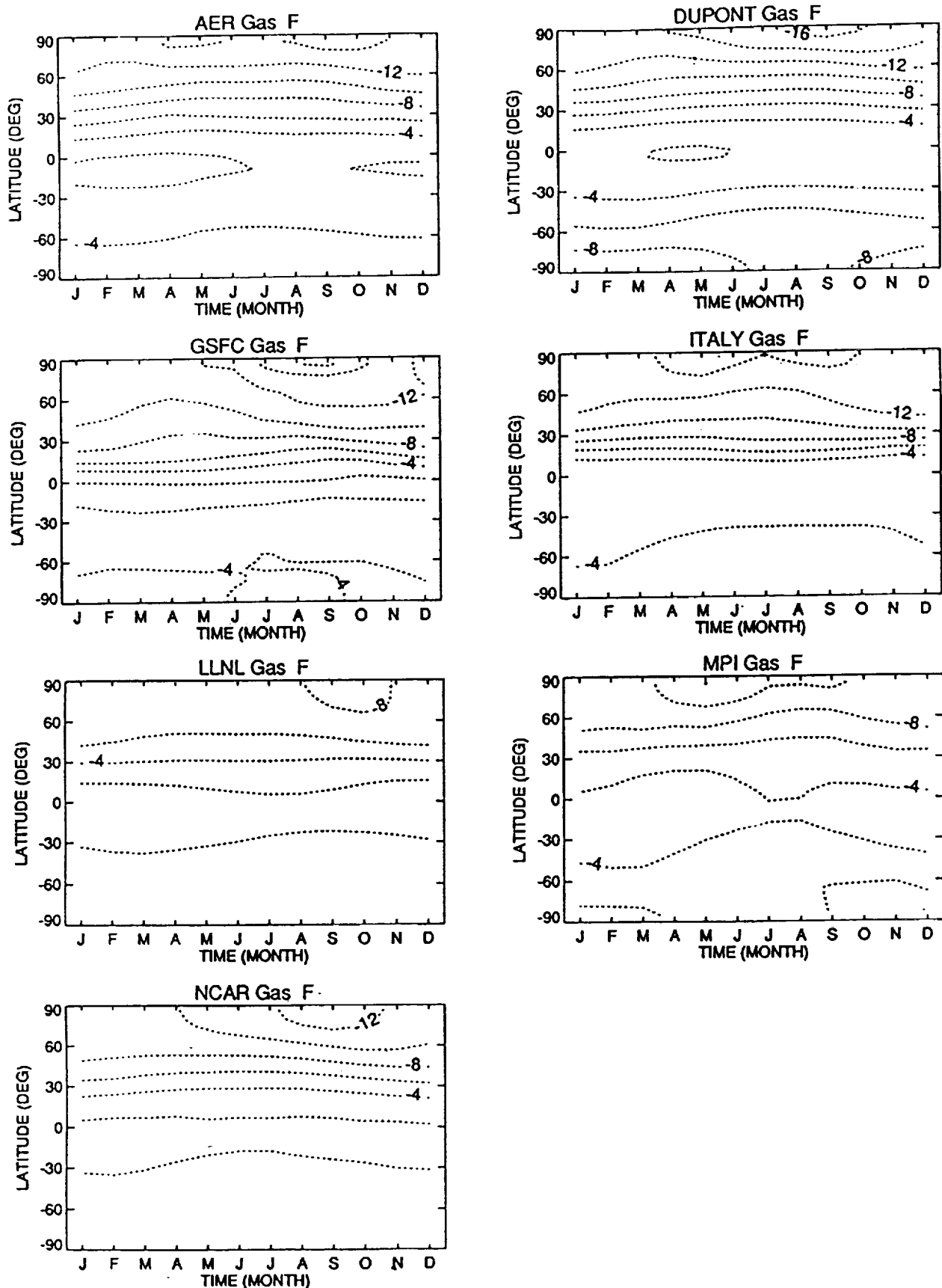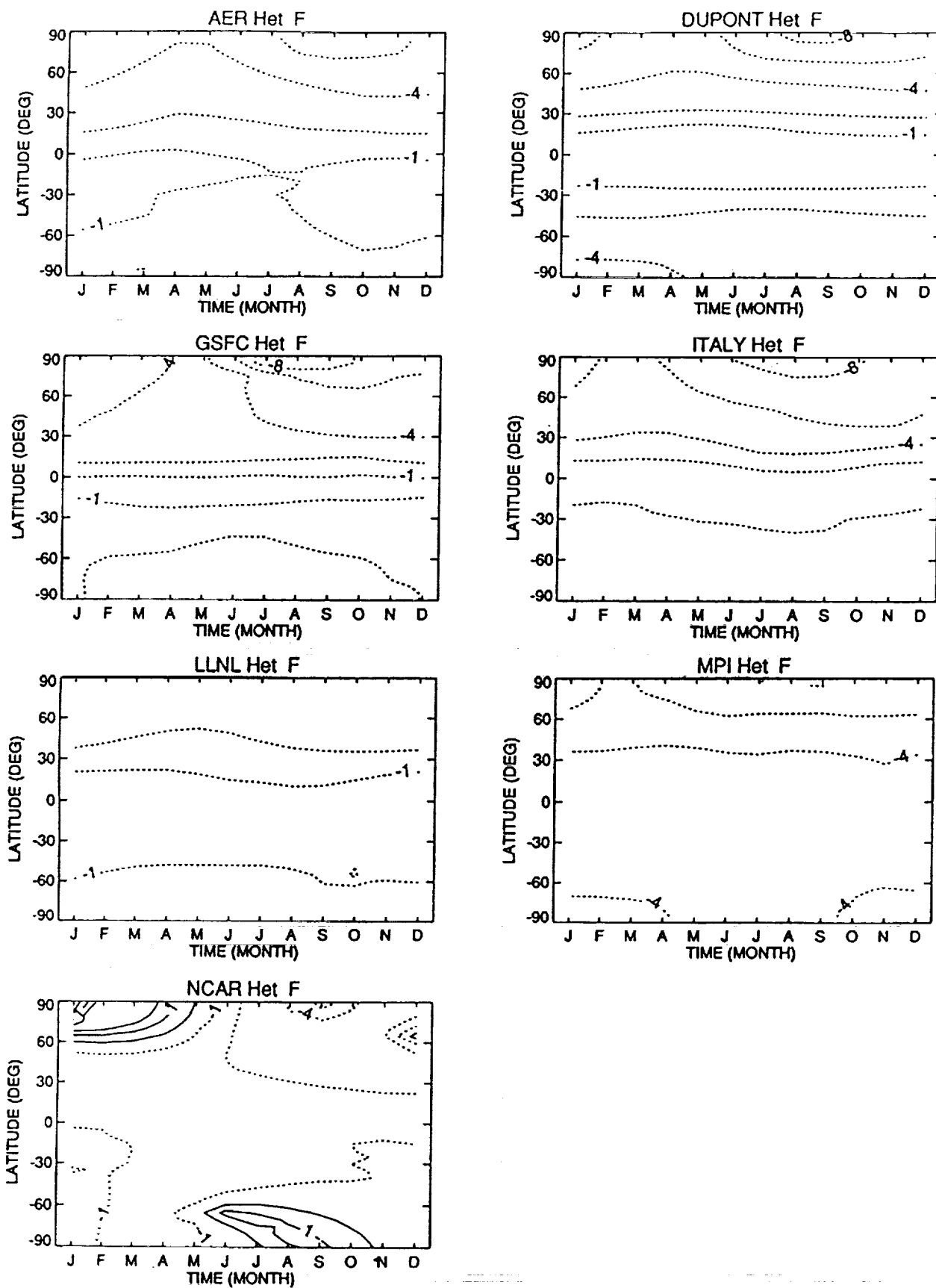
Figure 8b. Calculated percent change in the column abundances of O_3 for the different models as functions of latitude and season in scenario G relative to the baseline (BSE) for case II. The contours are +0.2, +0.1, 0, -0.1, -0.2, and -0.4%.

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Figure 9a. Calculated percent change in the local concentration of O_3 for the different models as functions of latitude and height in scenario A relative to the baseline (BSE) for case I. The contours are +4, +3, +2, +1, 0, -0.5, and -1.0 to -9 in steps of 1.0%.

Figure 9b. Calculated percent changes in the local concentration of O_3 for the different models as functions of latitude and height in scenario A relative to the baseline (BSE) for case II. The contours are +4, +3, +2, +1, 0, -0.5, -1.0, -2.0, -3.0, and -4.0%.
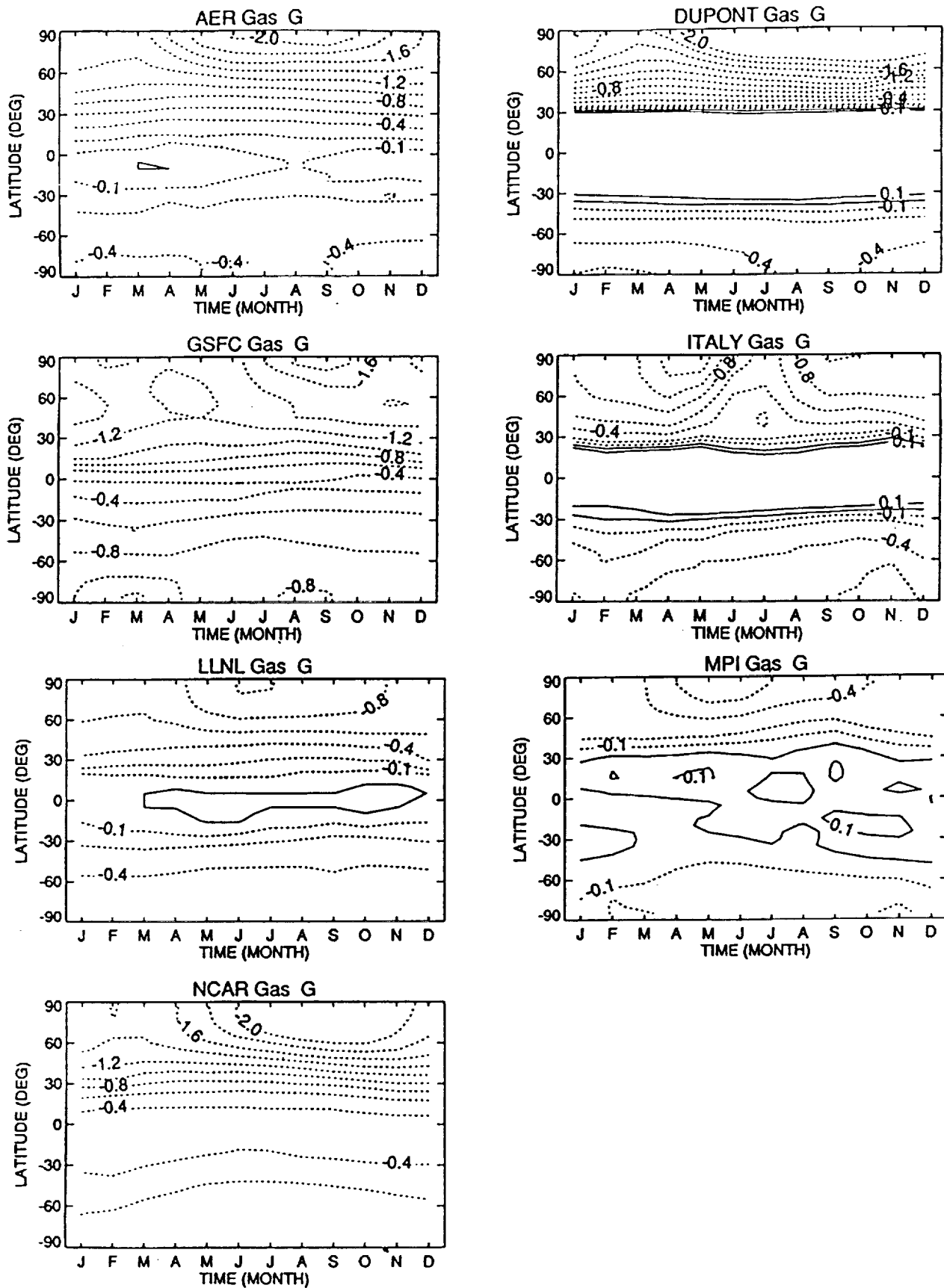
Figure 10a. Calculated percent changes in the local concentration of O_3 for the different models as functions of latitude and height in scenario F relative to the baseline (BSE) for case I. The contours are +3, +2, +1, 0, -2.0, -5.0, -10.0, and -15.0%.
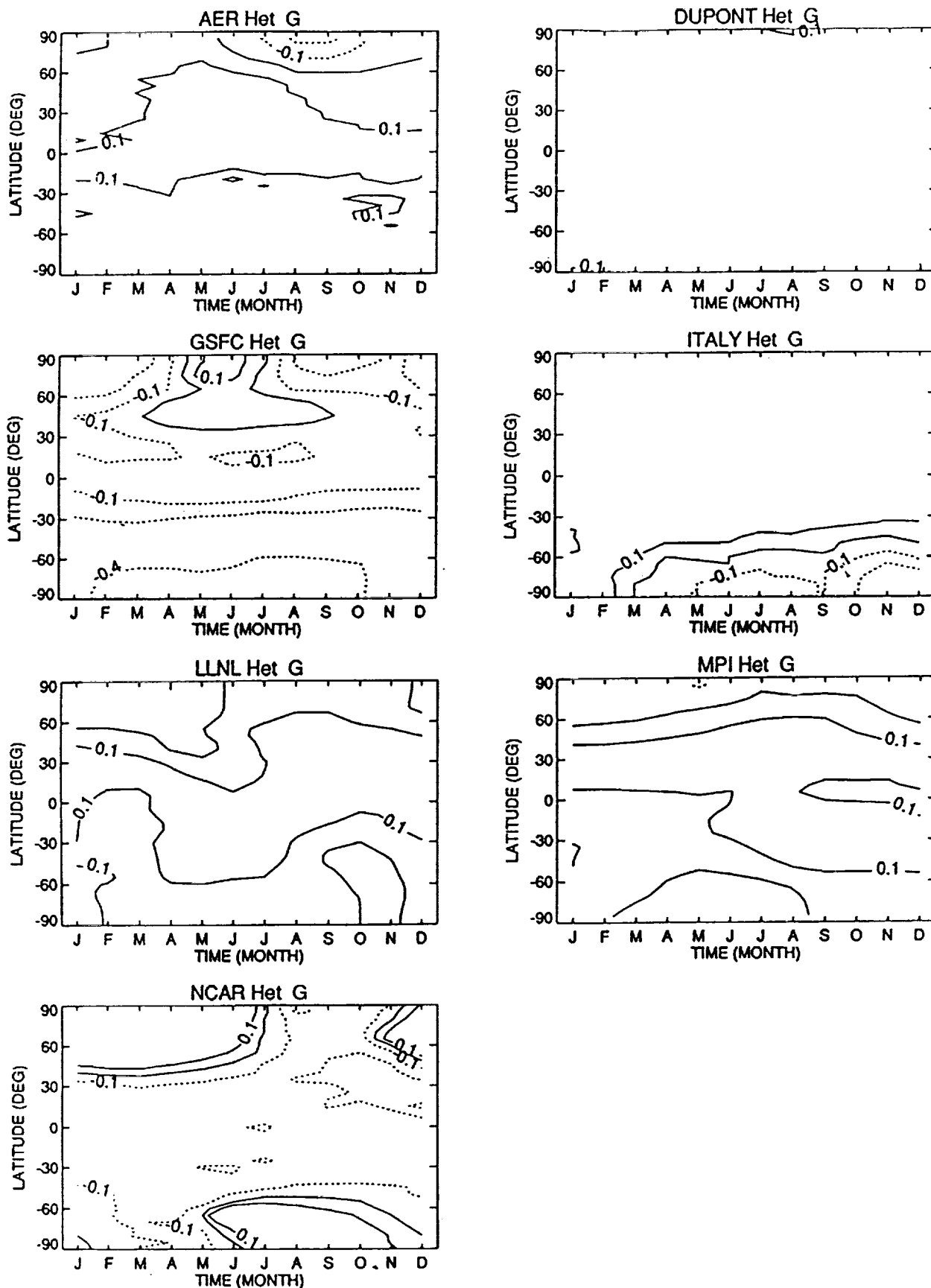
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Figure 10b. Calculated percent changes in the local concentration of O_3 for the different models as functions of latitude and height in scenario F relative to the baseline (BSE) for case II. The contours are +3, +2, +1, 0, -2.0, and -5.0%.

Figure 11a. Calculated percent changes in the local concentration of O_3 for the different models as functions of latitude and height in scenario G relative to the baseline (BSE) for case I. The contours are +1.0, +0.5, 0, -0.5, -1.0, -1.5, and -2.0%.
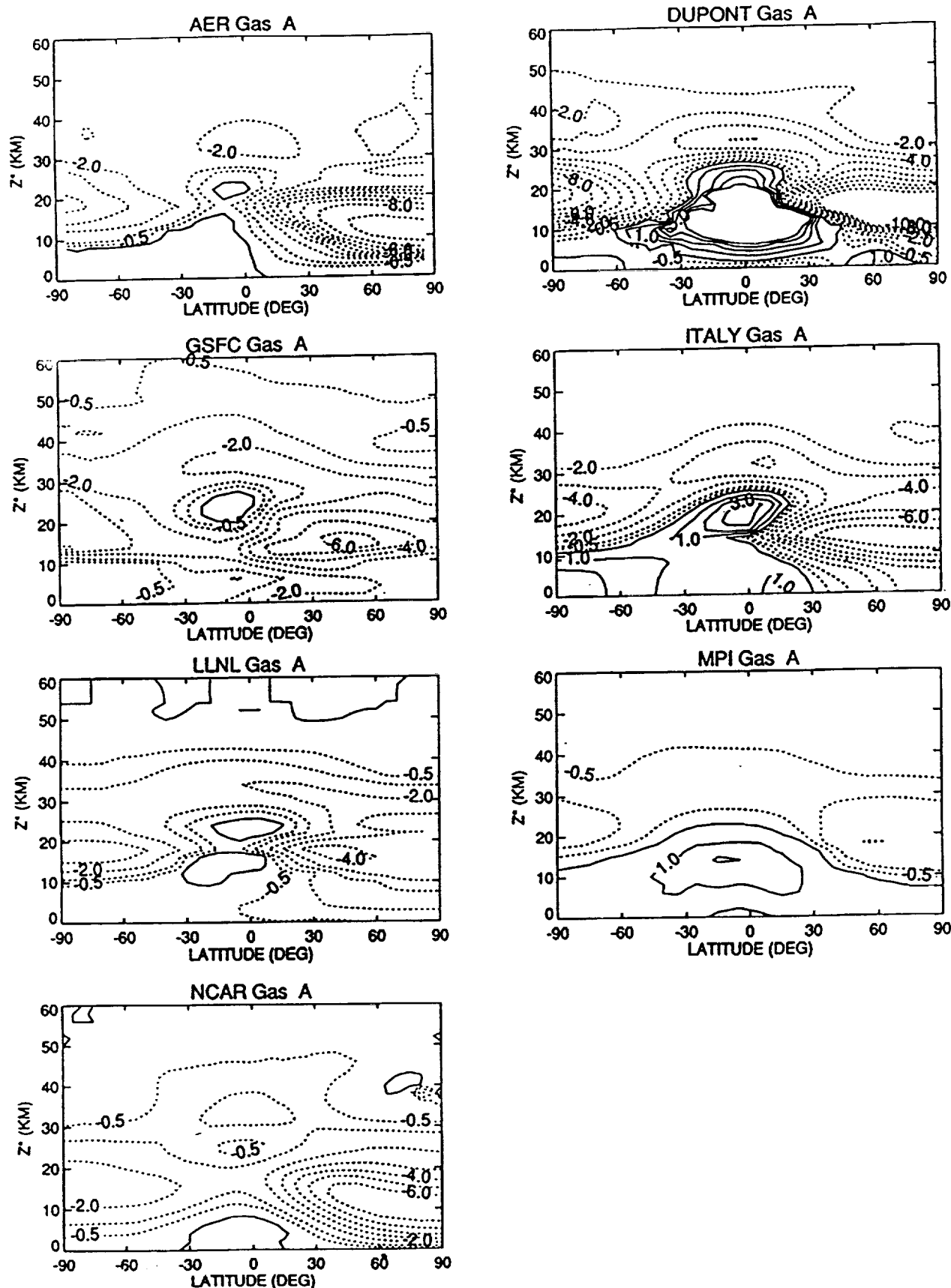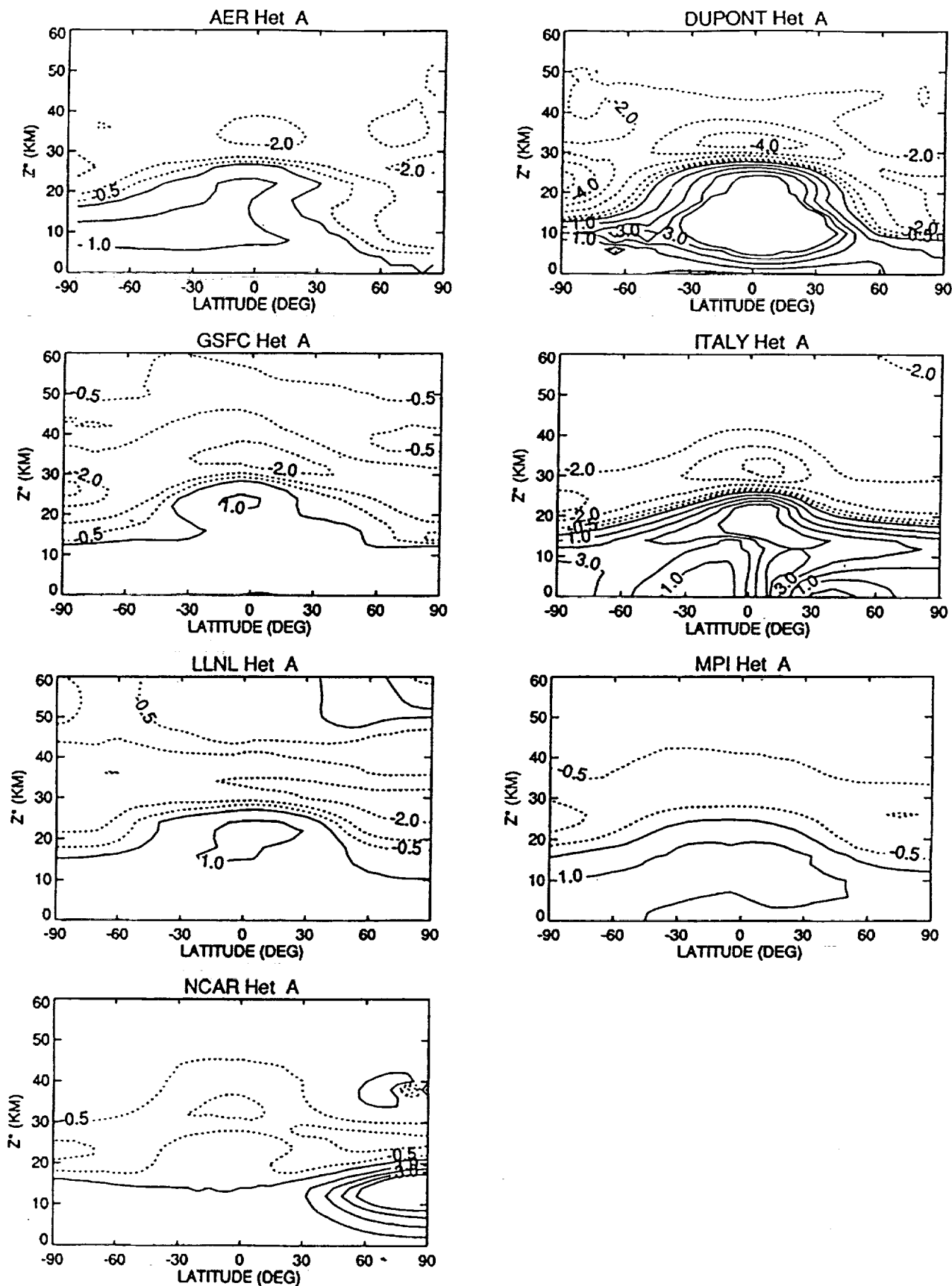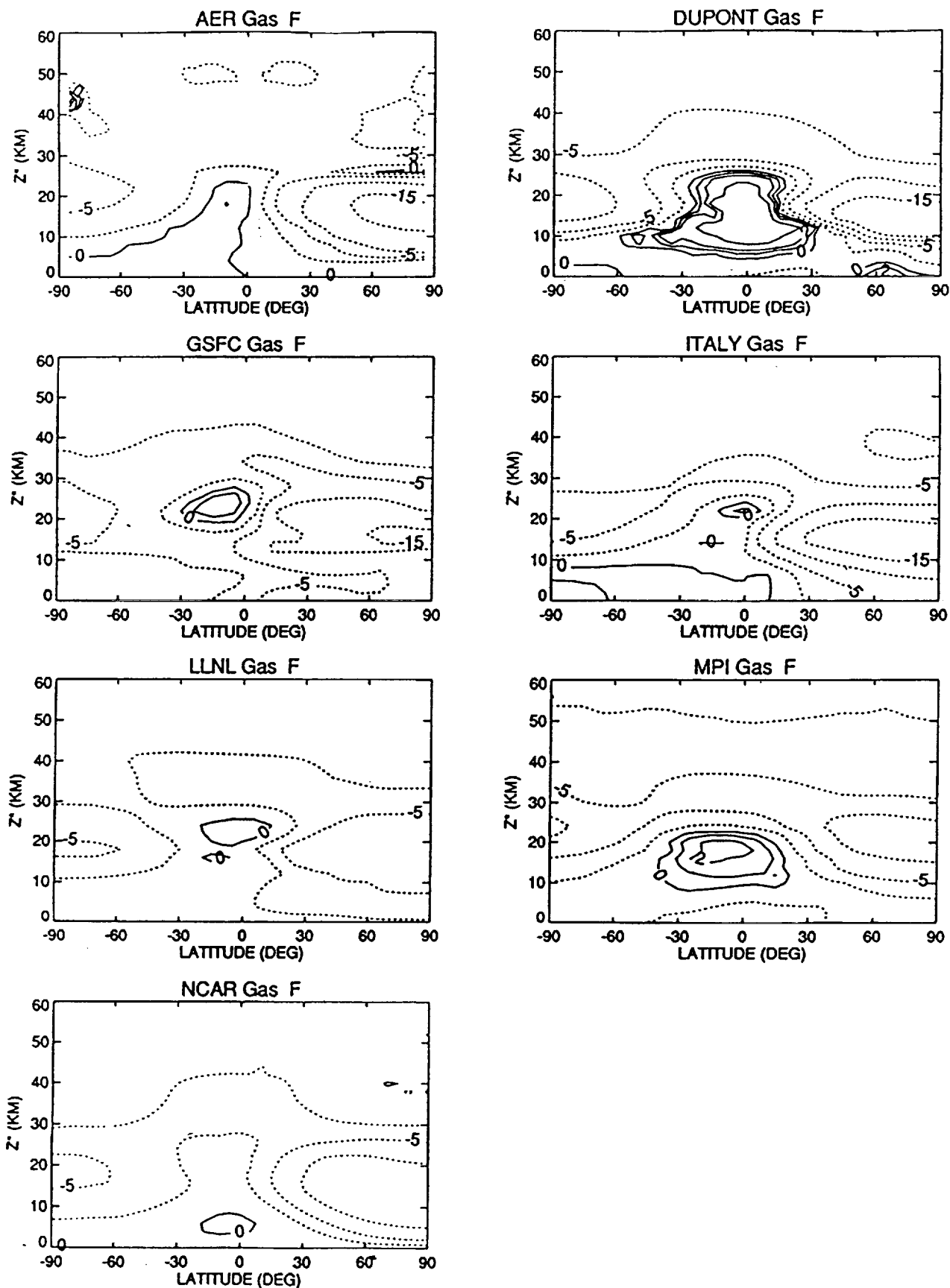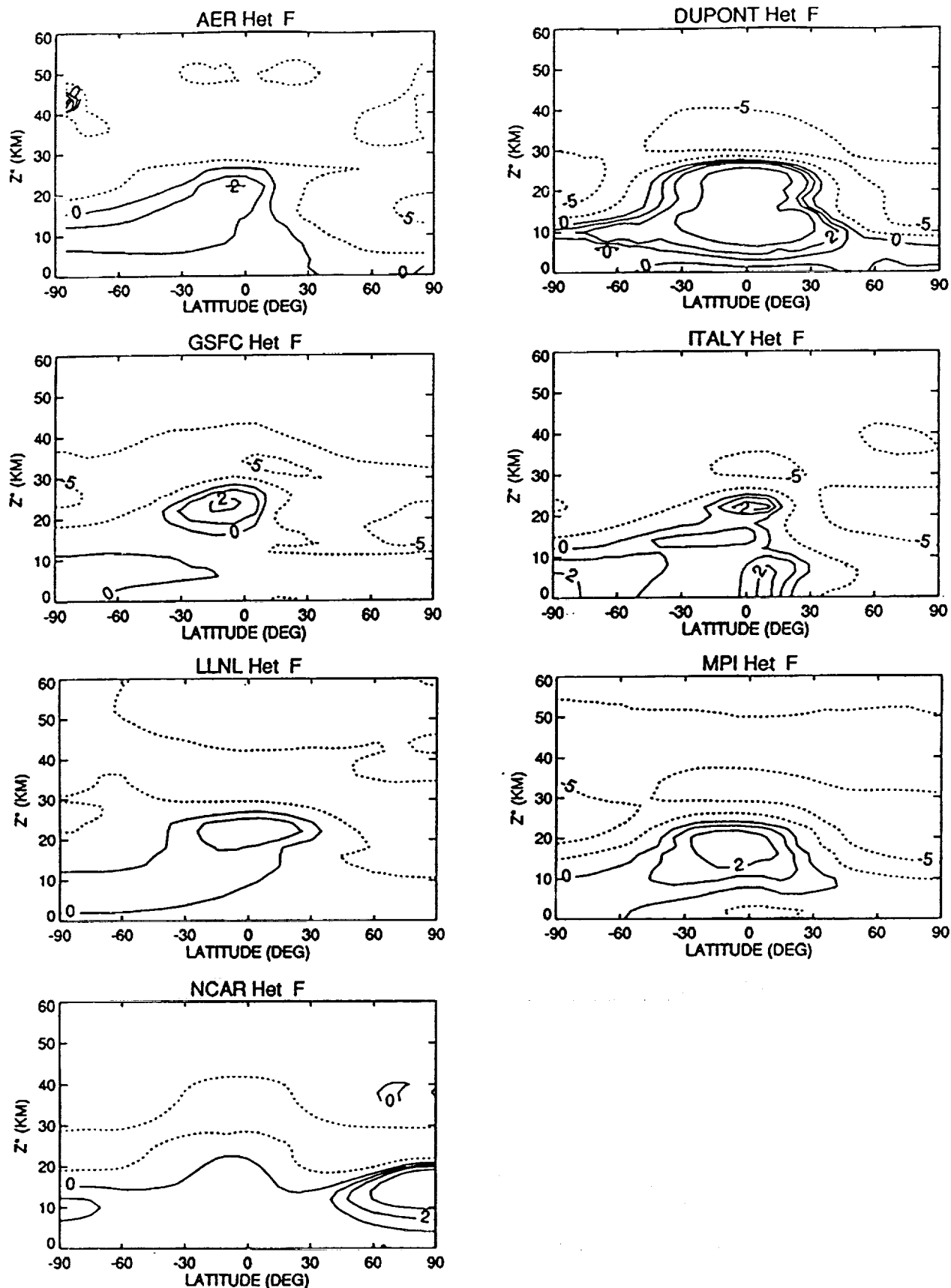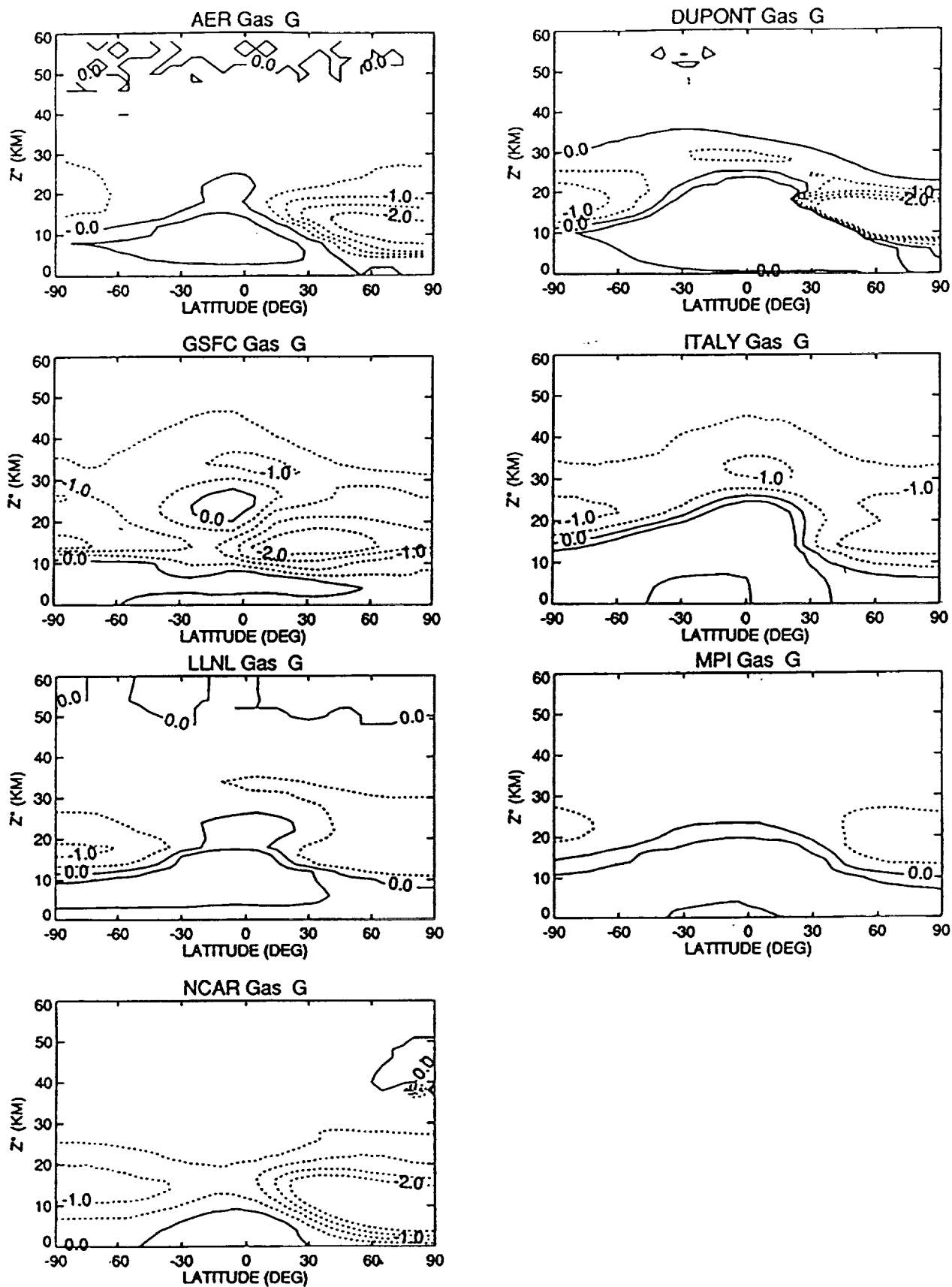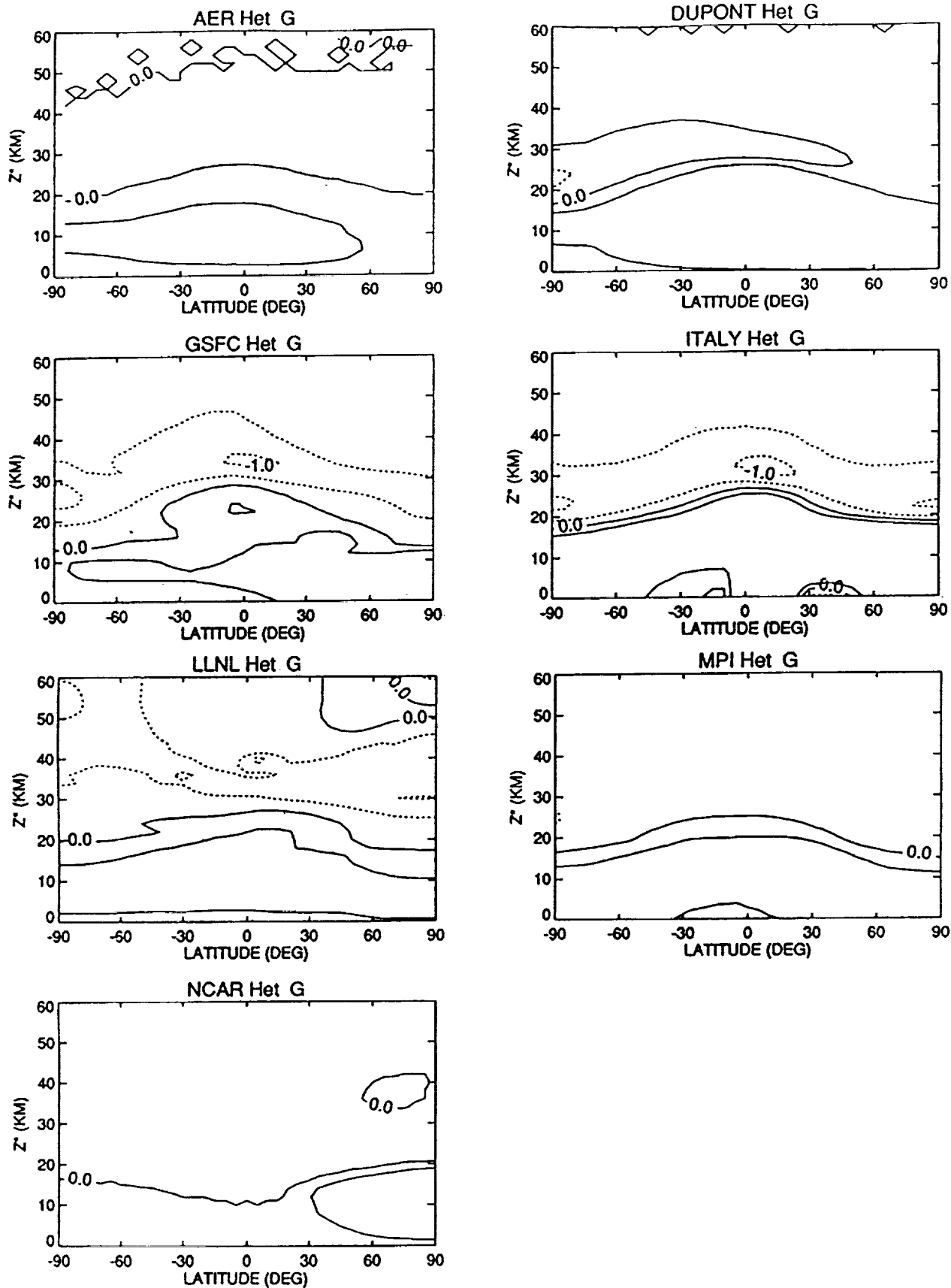
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Figure 11b. Calculated percent changes in the local concentration of O_3 for the different models as functions of latitude and height in scenario G relative to the baseline (BSE) for case II. The contours are +1.0, +0.5, 0., -0.5, and -1.0%.

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Chapter 6

A Brief Report of Interim Results from AASE-II with Respect to HSRP/AESA Studies

Contributions from the AASE-II Principal Investigators,
edited by M. J. Prather

OVERVIEW

The Airborne Arctic Stratospheric Expedition II (AASE-II) was planned as a major study of the 1991/92 winter Arctic stratosphere using the NASA ER-2 and DC-8 aircraft. The initial program sponsors were the Upper Atmosphere Research Program of NASA along with National Oceanic and Atmospheric Administration (NOAA), National Science Foundation (NSF), and the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS). The plan was to fly the DC-8 (altitude range 0 to 13 km) and the ER-2 (altitude range 15 to 20 km) concurrently from October 1991 through March 1992, thereby providing a unique opportunity for HSRP/AESA to gather the measurements necessary for its assessment of high-speed civil transports (HSCTs), i.e., predicting the impact of aircraft exhaust from a future fleet of supersonic aircraft that would cruise in the stratosphere between 15 and 20 km.

HSRP/AESA supported part of the basic mission costs for AASE-II, including flight hours for the ER-2 and DC-8 to address topics specific to AESA needs. In addition to this general support, AESA specifically solicited DC-8 measurements of a suite of trace gases: N_2O, CH_4, CO, and CO_2 (PIs: Sachse and Anderson); NO, NO_2, NO_y, and O_3 (PIs: Ridley, Weinheimer, and Walega); halocarbon and hydrocarbon grab samples (PIs: Blake and Rowland); H_2O (PI: Kelly); and Particle Spectrometer and Impactors (PI: Pueschel). From the point of view of AESA, these in-situ measurements provide essential continuity into the troposphere of the almost identical suite of trace gases as on the ER-2. In this way we hope to be able to characterize the transport and chemistry both above and below the region of projected high-speed civil transport flight.

We review the initial scientific goals of AESA participation in AASE-II and present a snapshot of preliminary AASE-II results. We also include a verbatim copy of the end-of-mission statement prepared by the AASE-II science team in March 1992. This mission statement summarized the scientific findings (e.g., the evidence for heterogeneous processing of NO_x by the sulfate-layer aerosols), but must be regarded as preliminary. Our understanding continues to evolve as we analyze the AASE-II measurements. The examples given here pre-date the publication of the scientific papers analyzing these observations and are intended as an overview of some of the experiments. The wealth of information on the stratosphere and upper troposphere from this combined ER-2/DC-8 mission still requires extensive analysis by the experimenters and will subsequently provide fundamental tests for the assessment models.

SCIENTIFIC GOALS

HSRP/AESA recognizes that the primary goals of AASE-II were directed towards polar ozone. (For a description of mission goals, see the AASE-II Handbook.) Nevertheless, by augmenting the DC-8 payload and by redirecting a few of the mission flights for both ER-2 and DC-8, HSRP could acquire important new atmospheric measurements that directly address elements in the assessment of HSCTs. Four principal scientific objectives for HSRP participation in AASE-II were clearly defined:

- Extend observations of tracer correlations (N_2O, O_3, NO_y, H_2O) from ER-2 flight levels (15-20 km) down to the tropopause (8-12 km) with DC-8 measurements in situ.

The linear correlation of tracers such as N_2O and NO_y over a large dynamic range was a surprising result from the first Antarctic Airborne Ozone Experiment (AAOE). Data from the Stratosphere-Troposphere Exchange Project (STEP) (tropical mission) and the first Arctic campaign (AASE-I) have continued to expand our empirical analysis of tracer correlations. The DC-8 in situ data on AASE-I (NO_x, NO_y, O_3, H_2O) did not include a true stratospheric tracer (N_2O). These relationships (e.g., N_2O - NO_y) tell us about transport and chemistry in the stratosphere.

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- Include simultaneous measurements of H_2O and CH_4 throughout the lower stratosphere and across the tropopause.

As part of AASE-II, the ER-2 measured H_2O, CH_4, and particles simultaneously at high frequency for the first time; the same measurements were part of the DC-8 in situ package (but H_2O failed). These measurements allow us to examine the role of physical processes as sources/sinks for H_2O in the lower stratosphere in addition to chemical enhancement from CH_4 oxidation. Concurrent particle measurements help identify the heterogeneous mechanisms controlling water vapor (including the impact of aircraft injections of H_2O).

- Identify emission signatures of present subsonic aviation in and near flight corridors in the lower stratosphere.

The current commercial fleet could serve as a low-altitude analog for future HSCT emissions (CO_2, H_2O, and NO_x) and may be an important perturbation to atmospheric composition and chemistry today. The in situ DC-8 measurements [CO_2, H_2O, NO_y and $NO_x(=NO+NO_2)$, soot] could be used to identify net perturbations along flight corridors. Pending more complete analysis, information could also be obtained on the rate of dilution and dispersion of emissions within flight corridors; these are key factors in understanding the fate of future HSCT combustion products at higher altitudes.

- Examine the interface between stratosphere and troposphere, particularly NO_x chemistry and its impact on O_3 tendencies.

The mixing of stratospheric air (dry, high ozone, low NO_x-high NO_y) with tropospheric air (wet, low ozone, low NO_y, high CO) combines two parcels with extremely different photochemical tendencies for O_3: under stratospheric conditions, addition of NO_x (e.g., from aircraft) tends to decrease ozone, whereas in the upper troposphere it enhances ozone. Data from AASE-II extend the AASE-I measurements to a different season and with substantially greater coverage of chemically active trace gases (CO and hydrocarbons).

In summary, through participation in the AASE-II mission, HSRP seeks a deeper understanding of tracer distributions in the lower stratosphere and across the tropopause, looks for evidence of the current aircraft fleet within the polar stratosphere, and will use these observations to aid in modeling and (if HSCTs are built) in tracing the emissions from high-flying aircraft. A more focused study of the NO_x-HO_x-ClO chemistry is planned as Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE), a dedicated HSRP campaign (November 1992 and May 1993).

BRIEF CONTRIBUTIONS

1. N_2O-CH_4-CO-CO_2 Correlations across the Tropopause
(G. Sachse, B. Anderson, and J. Collins)

Continuous in situ measurements of the tracer species CO, CH_4, N_2O, and CO_2 were provided by an instrument that consisted of three tunable-diode-laser (TDL) gas detection channels (CO, CH_4, and N_2O) and a CO_2 nondispersive infrared channel. For the AASE-II configuration, its temporal response was about 10 sec (dictated by the sample flow rate) and its measurement precisions (2 σ) were CO (2 ppb), CH_4 (0.3%), N_2O (0.3%), and CO_2 (0.1%). Calibrations were performed at frequent intervals (15-30 min) during each flight using multi-component Niwot Ridge (NOAA) calibration standards. In total, over 170 hours of measurements were recorded

during the January, February, and March flight series, which substantially increased the available databases for these species in the lower stratosphere/upper troposphere of the northern latitudes.

Figure 1a-c shows the scatter plots of CH_4, CO, and CO_2 versus N_2O for the stratospheric observations of the flight of 12 March 1992. Preliminary analyses based on these and other flight data indicate: (1) concentrations of CH_4 and N_2O in the northern middle latitude lower stratosphere are so highly correlated that either may be used as a tracer of the circulation, (2) plots of N_2O versus potential temperature indicate the presence of chemically aged (i.e., N_2O poor) air beneath the polar vortex at DC-8 flight altitudes of about 12 km, (3) aircraft plumes are devoid of significant N_2O enhancements which makes this species a "control" for meteorological variability when looking for enhanced CO, CO_2, or NO_x associated with current aircraft corridors, and (4) the CO_2 measurements are accurate enough to be useful as an independent tracer of stratospheric dynamics.

2. NO_y-O_3 Correlations from the DC-8
(A. Weinheimer)

In situ measurements of NO, NO_2, NO_y, and O_3 were made using three parallel NO-chemiluminescence detectors (PIs: Ridley, Weinheimer, and Walega). Sampling at 2-second intervals can be averaged over 1 minute for better precision. The relationship between NO_y and O_3 is well known from the ER-2 flight data (PI: Fahey; PIs: Proffitt and Margitan); however, observations in the lower stratosphere are limited to brief periods of climb/descent during takeoffs/landings. The new DC-8 measurements for the flight of 17 February 1992 shown in Figure 2, greatly extend our understanding of the lower stratosphere. With the exception of the tropics, the ratio NO_y/O_3 increases from 0.003 at peak ER-2 altitudes of about 20 km to about 0.005 at DC-8 flight levels. Because NO_y is conserved (outside of polar regions with denitrification), this change represents loss of O_3 as middle latitude stratospheric air descends and approaches the tropopause. The correlation in such scatter plots is a critical test of the stratospheric models' circulation and ozone chemistry. The upper troposphere (O_3 less than 100 ppb in Figure 2) shows much large scatter and no obvious correlations of NO_y with O_3. Further study of this latter region near the tropopause will be important in assessing the impact of aircraft NO_x ($NO+NO_2$) on tropospheric ozone.

3. Hydrocarbons and Halocarbons across the Tropopause
(D. Blake and F. Rowland)

During each of the 19 flights of the DC-8 during AASE-II, 72 whole air samples were collected (PIs: Blake and Rowland). After landing, the 2-liter stainless steel canisters were transported to the laboratory at UC Irvine and the contents assayed for selected halocarbons and nonmethane hydrocarbons (NMHCs). Vertical profiles of five NMHCs and three halocarbons obtained during the 20 February 1992 descent into Bangor, Maine, are seen in Figures 3a and 3b. The mixing ratios from troposphere to stratosphere of all the NMHCs decreases significantly. (The JPL microwave temperature profiler [PI: Gary] determined the altitude of the tropopause.) However, there was still more than 100 ppt of ethane (C_2H_6) above 12 km, suggesting that it may play a role in stratospheric chemistry other than just rapid, irreversible photochemical destruction. Although the corresponding halocarbon concentrations do not display such large relative decreases across the tropopause, a significant fraction of each of these gases has been lost, and their relative destruction rates can be used to derive a photochemical aging of the air parcel.

4. MTP Resolution of the Tropopause
(B. Gary)

The microwave temperature profiler (MTP, PI: Gary) was a new instrument on the DC-8 (it had flown on the ER-2 in this and previous missions). By measuring the vertical temperature gradient above and below the DC-8 flight level, the lapse rate can be derived and the boundary between stratosphere and troposphere delimited. Figure 4 shows both the DC-8 flight level for 17 February 1992 (920217) and the tropopause height calculated from the MTP. The in situ samplers were in the stratosphere for two periods (46,000 to 49,000 sec UT, and 52,000 to 70,200 sec UT). During the first period, the outside air temperature could not have been used to determine the aircraft position relative to the lower stratosphere. At this time, conditions were especially favorable for the MTP to produce reliable measurements of the tropopause location. These results have helped in the analysis of the impactor samples (i.e., the large particles at 10.5 km represent volcanic aerosols) and the hydrocarbon and halocarbon grab samples can be placed in terms of potential temperature relative to the tropopause. The MTP further provides a unique capability for measuring turbulence and wave-breaking events near the tropopause.

5. CFC-11 and CFC-113 from the ER-2
(J. Elkins and D. Fahey)

A new instrument, the Airborne Chromatograph for Atmospheric Trace Species (ACATS), was developed for the AASE-II and is located in the Q-bay of the NASA ER-2 aircraft. ACATS (PIs: Elkins and Fahey) is a gas chromatograph that includes a sensitive electron capture detector and is optimized for fast response measurement of atmospheric chlorofluorocarbon-11 (CFC-11 or CCl_3F) and CFC-113 (CCl_2F-$CClF_2$) once every 2 minutes. Addition of these two CFC molecules to the complement of species already measured on the ER-2 platform offers new scientific opportunities. Atmospheric CFC-11 and -113 are important ozone-depleting chemicals, which together represent about 30% of the total organic chlorine in the atmosphere. The use of high-resolution CFC measurements along with correlations between different tracers generated by dynamic models permits calculation of the total organic chlorine over the complete flight. The decay of the CFCs in older, more chemically aged air is a combination of both photochemical loss and the lower concentrations in the troposphere in previous years. The total amount of CFCs in the stratosphere as well as the effective lag in their photochemical loss are very important factors in the empirical determination of lifetimes from knowledge of emissions and surface monitoring.

The CFC molecules are excellent tracers of stratospheric dynamics. A sharp decrease in CFC mixing ratios was observed on the ER-2 aircraft flight of 16 January 1992 in a region where ClO (PIs: Toohey and Avallone) mixing ratios increased (see Figure 5a). This sharp decrease delineates the extent of the polar vortex and, coincident with the ClO increases, confirms the theory that destruction of CFCs releases chlorine that in part goes into ClO. Linear correlations are found for molecules with similar lifetimes or at altitudes where the local lifetimes are greater than the time scales of vertical transport. A cross plot of CFC-113 versus CFC-11 (Figure 5b) shows a strictly linear relationship for CFC-11 mixing ratios greater than 50 ppt, with considerable curvature at lower values where CFC-11 is more rapidly destroyed than CFC-113. ACATS is a versatile instrument that will be utilized in the SPADE and future polar missions; it can be easily modified to measure stratospheric CCl_2F_2, CH_3CCl_3, CCl_4, CO, CH_4, N_2O, and $CHClF_2$ (HCFC-22).

6. ClO, BrO and Heterogeneous Chemistry
(D. Toohey and L. Avallone)

The ClO/BrO instrument (PIs: Toohey and Avallone) was modified slightly from the previous mission (AASE-I) in order to perform diagnostic tests that would reduce the absolute uncertainty of

the measurements. From in-flight tests--including velocity profiles within the detection regions, reagent NO flow variations to elucidate the degree of inhomogeneity of mixing, and bulk flow velocity scans to determine the ozone correction--we have been able to substantially reduce the uncertainties in chemical conversion of ClO to Cl atoms. Addition of lab tests carried out before and after the mission further refined the absolute calibrations. Since these tests were also carried out with the instrument configured as during the AAOE and AASE-I missions, measurements for 70 or more flights of the ER-2 ClO/BrO instrument can be reported on the same calibration standard. Thus, detailed comparisons--for example changes due to Pinatubo aerosol--will be more meaningful.

Three flights of the ER-2 during AASE-II occurred in the late afternoon, providing sunset profiles for key radicals, including ClO and BrO. Of these, two were test flights in the late summer of 1991; the third was a transit flight from Bangor, Maine, to Moffett Field, California, in late March. Figure 6a shows 150-second averages of ClO obtained on 26 March 1992, with an overlay of an averaged ClO profile from February 1988 over Moffett Field (solid line, Brune et al.). The rate of ClO disappearance after sunset is a sensitive indicator of NO_2 concentrations, since ClO reacts rapidly with NO_2 to form $ClONO_2$ at middle latitudes. The results from the two test flights in late summer agree well with those from February 1988, but differ markedly from those of March 1992, indicating substantially less NO_2 on the latter flight. A photochemical model indicates that 200 ppt of NO_2 at high sun angles are required to match the ClO profile from 920326 (see Figure 6a). This is consistent with inferred NO_x from measurements of Fahey and is half as large as values inferred by Brune et al. from their 1988 measurements. All of these results are consistent with the behavior expected from heterogeneous chemistry, especially the hydrolysis of N_2O_5, and should increase our confidence in the coupled chemistry of ClO_x and NO_x in the lower stratosphere.

Significantly perturbed chemistry near the subtropical jet was observed on the flights of 920112 (Figure 6b) and 920322. In both cases ClO enhancements were found at the lowest temperatures in the dive regions at mid-flight. In one case a change in the particle distribution was observed by the FSSP. These results indicate that a PSC-type chemistry can occur at low latitudes and highlight the need to examine the possibility for perturbed chemistry in the exhaust plumes of both subsonic and supersonic aircraft, especially when flying in cold region of the atmosphere.

Perhaps the most striking result from the AASE-II mission was the consistently high abundances of ClO at middle latitudes, before and after the appearance of PSCs in the polar vortex. These measurements and model calculations for gas-phase and heterogeneous chemistry at different latitudes are summarized in Figure 6c. This result, correlated with the low ratio of NO_x to NO_y, has demonstrated that either heterogeneous reactions on sulfate aerosols play a dominant role in the balance of ClO_x and NO_x in the lower stratosphere or our current understanding of gas-phase chemistry is severely lacking. Photochemical models incorporating the hydrolysis of N_2O_5 on sulfate aerosols agree well with the observations, providing support for the former interpretation. Further examination of the entire ClO data set, including balloon profiles before and after the eruption of Mount Pinatubo, should help to solidify this conclusion.

Significant improvements in optical baffling since AASE-I have led to increased sensitivity by factors of about two for chlorine detection and three to five for bromine detection. With minor NO injector modifications we are now able to cycle NO every 16 seconds, rather than 32 seconds as in the past. Beginning in December, ClO measurements were reported every 16 seconds with a detection limit of 3 ppt. BrO measurements require an integration of about 15 minutes for better than 2 ppt precision, whereas 45 minutes or greater were required for the same sensitivity in past missions. Throughout the AASE-II mission the BrO results were roughly consistent with previous measurements and in good agreement with the variations expected from known chemistry of bromine in the stratosphere. More detailed conclusions await further analysis.

7. HCl and the Budget for Inorganic Chlorine
(C. Webster and R. May)

A new infrared laser absorption spectrometer on NASA's ER-2 aircraft has made the first in-situ measurements of the principal chlorine reservoir hydrochloric acid (HCl) in the lower stratosphere, with simultaneous measurement of the atmospheric tracers N_2O and CH_4 (ALIAS, PI: Webster). Data from numerous flights in the lower stratosphere near 20 km from August 1991 through March 1992 during AASE-II have revealed a close negative correlation of HCl with these tracers, which varies systematically with latitude over the sampled range of 20N to 90N. Figure 7 shows the average observed HCl-N_2O relationship at ER-2 flight levels and includes total Cl_y versus N_2O inferred from the whole air samples (PIs: Heidt and Vedder) of chlorocarbon source gases; model predictions of $ClONO_2$ are also shown. Dramatic differences are seen between the observations and 2-D models using gas-phase-only chemistry. In particular, volume mixing ratios of HCl at high latitudes in October are about half that of the gas-phase model predictions. At low latitudes, observed HCl amounts are much closer, about 15% lower than predictions. In addition, the observed variation of decreasing HCl with increasing latitude is opposite to the model predictions which show an HCl amount increasing with latitude due to the reduced insolation towards the pole. These gas-phase-only models seriously underpredict the ration of HCl to ClO measured simultaneously on the ER-2.

Contrary to earlier belief, HCl is not the principal reservoir of inorganic chlorine (Cl_y) in the lower stratosphere; it represents only about 25% of the Cl_y at high latitudes at ER-2 flight levels and only about 40% at low/middle latitudes. The low/middle latitude HCl measurements and the measured ratios of ClO/HCl are better matched with models incorporating heterogeneous chemistry on sulfate aerosols. Nevertheless, the low HCl measurements at high latitudes in warm air with low aerosol surface areas indicate that the apparent discrepancy in the chlorine budget may be due to inadequate representation of the gas-phase chemistry, such as an unidentified chlorine reservoir, errors in the photolysis rate of $ClONO_2$, or underestimation of the OH concentrations.

8. Sulfate Aerosols and Heterogeneous Chemistry
(J. Wilson)

The focused cavity aerosol spectrometer (FCAS; PI: Wilson and Ferry) and condensation nucleus counter (CNC; PI: Wilson) permit characterization of the aerosol size distribution in the diameter range from 0.01 to 2 μm. In AASE-II, these instruments characterized the aerosol resulting from the eruption of Mount Pinatubo. Aerosol surface, number and volume concentrations, and mean sizes varied throughout AASE-II. Aerosol properties varied with location and time. These measurements provide insight into heterogeneous processes. For example, the hydrolysis of N_2O_5 on the surface of sulfate aerosol is expected to result in an increase of ClO at middle latitudes. Figure 8 shows data acquired on 17 September 1991 at middle latitudes. ClO (PIs: Toohey and Avallone) is plotted against aerosol surface area determined from the FCAS particle measurements. The model results were provided by M. Prather. Both the model and measurements show an increase in ClO for small increases in aerosol surface. The slope decreases at larger loadings. The data suggest that the aerosol surface affects the population of chlorine radicals and support the argument that heterogeneous processes are important in the stratosphere. The CNC and FCAS AASE-II aerosol data set must be analyzed in conjunction with the data describing reactive species and tracers for additional evidence concerning heterogeneous processes.

9. Mount Pinatubo Aerosols
(J. Dye, D. Baumgardner, and S. Borrmann)

The eruption of Mount Pinatubo dramatically increased the concentration and surface area of stratospheric aerosols. Measurements of particles larger than 0.4 μm diameter made with the FSSP 300 (PIs: Dye, Baumgardner, and Ferry) on the ER-2 during AASE-I, a volcanically quiescent period, can be compared in Figure 9 to measurements made during AASE-II after the eruption of Pinatubo. The top panel shows the measurements on 881231 (31 December 1988) from Wallops Island, Virginia (38N) to Stavanger, Norway (61N); the second panel, those from Moffett Field, California (37N) to 52N and back on 910917; the third panel, from Bangor, Maine (45N) to about 24N and return on 920322. The AASE-I observations were made during a period considered to be approximately at background levels in terms of stratospheric sulfate aerosol loading, and they are very uniform (top panel). During the 910917 flight and some of the October flights from Fairbanks (not shown), the particle concentrations are less than those found in 1988-89, suggesting that "background" was still decreasing. For example, the concentration of particles greater than 0.4 μm decreased from about 1 cm^{-3} on 881231 (A in top panel) to 0.5 cm^{-3} for 910917 (B in middle panel), and large particles with diameters from 0.6 to 1.0 μm decreased relatively more, from 0.2 cm^{-3} to less than 0.01 cm^{-3}. The 910917 observations show patchy regions (C in middle panel) in which concentrations are greatly increased by the volcanic plume. By March 1992 the distribution of stratospheric aerosol is again uniform, but now a factor of 10 greater than in 1988-89, and a factor of 20 greater than for the volcanically undisturbed region for 910917. Surface area was increased by a factor of 20 to 30 over much of the lower stratosphere by the eruption of Mount Pinatubo.

A preliminary analysis of these measurements has several implications for HSRP/AESA studies: (1) the decay of the larger sulfate particles in undisturbed regions between 1989 and 1992 raises questions about the "background" levels of sulfate aerosols (in the absence of volcanic activity) and the time constant for removal of volcanic aerosols; (2) natural, volcanically induced variations in the concentration and surface area of stratospheric sulfate particles are much larger than variations possibly induced on a global scale by the current aircraft fleet, although local enhancements by aircraft might be large; and (3) although the number of particles introduced by aircraft globally may be small compared to volcanoes, particulates from aircraft might influence the fraction of sulfuric acid particles that are liquid or solid, thereby influencing chemical partitioning. This topic is largely unstudied.

10. NO$_y$-N$_2$O, Looking for Aircraft Corridors
(M. Lowenstein, J. Podolske, and A. Weaver)

On 22 February 1992 the ER-2 flew south out of Bangor, Maine. On this flight at a constant altitude of about 18.5 km the aircraft encountered a region of large apparent enhancement in NO$_y$ (PI: Fahey) at about 34N latitude (UT of 50400 s in Figure 10a). To interpret these fluctuations in NO$_y$ (e.g., possibly as aircraft exhaust) required the simultaneous measurement of other trace species. By plotting the N$_2$O data (PI: Lowenstein) alongside the NO$_y$ data (Figure 10b), the enhanced NO$_y$ in this air mass correlated with low values of N$_2$O. The observed N$_2$O-NO$_y$ correlation is similar to previous aircraft observations at middle and high latitudes made away from denitrified regions. Thus, the enhanced NO$_y$ cannot be attributed to a local source, but rather from naturally aged stratospheric air. Such correlations of chemically active species with various long-lived tracers (N$_2$O, CFCl$_3$, CH$_4$, etc.) are expected to be an important tool in identifying aircraft exhaust in the stratosphere as well as a fundamental test for the global assessment models.

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11. Black Carbon Aerosols and Aircraft Exhaust
(R. Pueschel)

As determined by 20 impactor samples collected on ER-2 and DC-8 aircraft (PI: Pueschel), black carbon aerosol (BCA) mass loadings in the stratosphere average 0.8 nanograms per standard cubic meter (ng m^{-3}) or 0.01% of the total aerosol. In the upper troposphere the BCA fraction is much larger, 0.3%. The data were acquired by integrating the log-normal size distribution of both BCA (Figure 11a) and $H_2SO_4 \cdot nH_2O$ aerosols (Figure 11b). In order to present the BCA and H_2SO_4 size distributions in a compatible manner, we approximate the size of each BCA particle by that of a sphere of equivalent volume and fit a log-normal size distribution to both the BCA and H_2SO_4 aerosols (a procedure that underestimates the actual surface area of the BCA particles available for heterogeneous chemical reactions).

Figure 11c shows particle size distributions from a 920217 sample collected by the DC-8 at 11.3 km MSL just before descending into Bangor, Maine. Correlative measurements (e.g., temperature profiles) confirmed that this sample was collected in the lower stratosphere. Size distributions of BCA (curve B) and H_2SO_4 (curve A) are represented as log-normal by least-squares fitting. The sulfate is trimodal with a "background" aerosol mode at an effective radius of 0.06 μm, and two enhanced modes with radii of 0.2 and 0.8 μm which are attributable to Mount Pinatubo volcanic injections. The elemental carbon aerosol is unimodal with a radius of 0.07 μm. In this example the BCA concentration is 3×10^{-4} (0.03%) by number, 3.3×10^{-5} by surface area, and 5.8×10^{-6} by volume relative to the total (i.e., sulfate) aerosol.

The low BCA concentration in the stratosphere is commensurate with a source from the current commercial air traffic, given the following assumptions: the BCA emission index is 0.1 g of BCA per kg of fuel burned; 10% of current route mileage is flown above the tropopause; and the average BCA residence time in the stratosphere is about one year. Taking BCA into account, the mean single scattering albedo for stratospheric aerosols is about 0.99. The projected HSCT fleet could conceivably double the current stratospheric BCA and significantly reduce the single scattering albedo of stratospheric aerosols.

END OF MISSION STATEMENT - SECOND AIRBORNE ARCTIC STRATO-SPHERIC EXPEDITION AASE-II

This statement has been prepared by scientists of the second Airborne Arctic Stratospheric Expedition (AASE-II). The mission was staged over a period of eight months from Moffett Field, California; Fairbanks, Alaska; Anchorage, Alaska; Stavanger, Norway; and Bangor, Maine. The mission used two aircraft to study the lower stratosphere: a high altitude ER-2 aircraft for *in situ* observations and a long-range DC-8 for remote sensing observations. This summary represents the preliminary conclusions of the scientists at the end of the flight series.

The issue of ozone depletion is of widespread public concern. Hence, policy makers and the public should be kept abreast of the advances in scientific understanding. It is in this spirit that we report our provisional interpretation of new data concerning stratospheric ozone in the Northern Hemisphere. A comprehensive interpretation of our findings will be forthcoming after a series of scientific meetings and the publication of peer-reviewed scientific papers.

Background To The Mission

In 1985, a large and unanticipated decrease in the abundance of ozone over Antarctica was reported by the British Antarctic Survey. Public concern was heightened in 1988 and again in 1991 by ground and satellite observations that showed ozone at northern mid latitudes in the winter

had decreased 6-8% between 1979 and 1990. It is critical to recognize that while ozone exhibits considerable natural variability, decreases in ozone overhead without other offsetting atmospheric changes result in increased ultraviolet radiation reaching the Earth's surface. Biological and medical studies suggest that the accumulated exposure to these increases produce deleterious effects on mankind and other living organisms.

Predicting ozone loss in the Earth's stratosphere over the next decade requires detailed knowledge of both chemical and transport processes. Two types of scientific investigation provide guidance for policy decisions: (1) mechanistic studies linking cause and effect, which serve as the foundation of our ability to look forward in time, and (2) global-scale studies of trends of atmospheric change. Improved understanding of mechanism and process was the focus of the second Airborne Arctic Stratosphere Expedition (AASE-II).

The research phase described here, which began in August, 1991, is a continuation of eposodic aircraft flights into the antarctic, arctic and mid-latitude stratosphere. More than one hundred flights have been made during the last five years by the ER-2 and DC-8, encompassing all latitudes from the South Pole to the North Pole. Results from the first of these aircraft campaigns, the Airborne Antarctic Ozone Experiment (AAOE) over Antarctica in 1987, demonstrated that chlorofluorocarbons (CFCs) released into the atmosphere caused dramatic springtime ozone erosion over the Antarctic. Those studies pinpointed chlorine monoxide and bromine monoxide as the species responsible for controlling the *rate* of ozone destruction and further indicated the importance of polar stratospheric clouds (PSCs) in producing chemical transformations that facilitate such destruction. In 1989, the first Airborne Arctic Stratospheric Expedition (AASE-I) was staged from Stavanger, Norway. During that mission, ER-2 flights into the arctic stratosphere revealed that chlorine monoxide and bromine monoxide were present at concentrations comparable to those observed over Antarctica in 1987. However, since the degree of ozone loss depends both on the ClO/BrO concentrations and on the *duration* of the elevated levels, the shorter period of cold temperatures in the Arctic diminishes the impact on ozone.

AASE-II is comprised of four major program elements: a high altitude ER-2 aircraft, a long-range DC-8 aircraft, extensive meteorological predictions and analyses, which include an array of computational programs to correlate and interpret the aircraft observations, and finally, the Total Ozone Mapping Spectrometer (TOMS) on the Nimbus-7 satellite, which monitored the global distribution of total ozone. The instrument packages on the two aircraft measured an array of the chemical species and other atmospheric parameters that are associated with the mechanisms that determine the distribution of ozone.

Meteorological analyses from the NOAA National Meteorological Center (NMC) provided the historical context, analysis and predictive capability for temperature, pressure and wind fields for the northern hemisphere during the field deployment.

Three questions define the principal mission objectives for AASE-II:

1.Will significant erosion of stratospheric ozone occur over the Arctic as stratospheric chlorine levels increase during the next decade?

2.What are the causes of mid-latitude stratospheric ozone decreases in late fall through early summer, revealed over the past decade by ground and satellite observations?

Finally, given the eruption of Mt. Pinatubo in June of 1991, we address another issue:

3.What effect do volcanoes have on the chemical processes that govern stratospheric ozone? In particular, could volcanic aerosols modify depletion of stratospheric ozone associated with industrial halocarbons?

AASE-II Summary Statement

- The chemical composition of the stratosphere was highly perturbed at northern latitudes this winter. Most of the chlorine released from CFCs in the stratosphere, where it resides as chemically stable inorganic chlorine (HCl and $ClONO_2$), was converted to the reactive form (ClO). This transformation, observed in a sequence of flights, began in mid-December and was complete by mid-January. Concentrations of ClO were observed by the ER-2 to increase during January, exceeding 1500 pptv on January 20th. Appearance of high ClO concentrations correlated with the disappearance of HCl and with the onset of temperatures cold enough to form polar stratospheric clouds (PSCs). The onset of cold temperatures, high ClO, and the loss of HCl had been predicted based on laboratory measurements and was observed simultaneously in specific air masses for the first time in AASE-II.

- Meterological conditions over the Arctic this winter were characterized by a period from mid-December to the third week of January when minimum temperatures dropped below the threshold for PSC formation at ER-2 altitudes. This period was shorter than average. An analysis of HCl, $ClONO_2$, NO, NO_2, $HONO_2$ and ClO concentrations from this mission, in the context of more than one hundred aircraft flights over the last five years, implies that ClO levels in excess of 1000 pptv should emerge at high latitudes in January during typical or colder years for the next two decades.

- Temperatures warmed abruptly within the vortex the third week of January. The decline of ClO commenced as expected when temperatures warmed above the PSC threshold. ClO dropped slowly: by mid-February concentrations from 700 to 1000 pptv were typical in the vortex. The decline of ClO continued into late March.

- Calculations based on the observed concentrations of HCl, $ClONO_2$, NO, NO_2, $HONO_2$, ClO and BrO in the arctic vortex in January and February indicate approximately 20% ozone removal between 15 and 20 km. Using data for ozone and tracers from the aircraft, evidence for comparable ozone removal was observed over a more limited altitude range. The percentage total column ozone loss is estimated to be about one half the percentage observed between 15 and 20 km. In the calculations, ozone removal is due in about equal measure to reactions involving chlorine and bromine.

- The amount of ozone destroyed in a given year is controlled by two factors: (1) total chlorine and bromine concentrations in the stratosphere, both of which are increasing annually; (2) the timing and vertical extent of temperatures below the threshold for PSCs. If temperatures had remained cold into the third week of February, which has occurred several times in the last decade, greater amounts of ozone would have been destroyed. The loss of ozone in winter 1991/1992, while significant, should not be described as an "ozone hole," a term coined to denote the sharp transition to dramatically suppressed O_3 levels over Antarctica. In this hemisphere, it is essential to focus on the more broadly distributed erosion of ozone at both mid and high latitudes.

- During 1992, the Total Ozone Mapping Spectrometer (TOMS) satellite measurements show that the hemispheric ozone average during January, February, and most of March was lower than any previous year in the TOMS record. TOMS measurements also showed that total ozone values in the mid-latitude maximum during February were 10-15% lower than any previous year in the TOMS record. The processes responsible for this ozone decrease are under investigation.

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• The mission revealed strong evidence for the influence of sulfate aerosols on stratospheric chemistry, particularly outside the polar vortex. Natural sulfate particles appear to suppress concentrations of NO and NO_2, leading to enhanced concentrations of ClO and BrO. The highest concentrations of ClO and BrO outside the vortex were observed in winter at high latitudes. The results are consistent with the view, expressed in the recent UNEP report, that ClO and BrO are likely to be implicated in recent reductions of column ozone amounts observed over midlatitudes. The largest changes in midlatitude ozone levels are observed in late winter and occur in the same altitude regions where ClO and BrO are elevated throughout the winter.

• The eruption of Mt. Pinatubo increased abundances of natural sulfate aerosol particles, potentially amplifying the effects of reactions which take place on the surfaces of particles. No significant direct injection of chlorine by the volcano was observed. There was no evidence for significant influence of Pinatubo aerosols on the chemistry of the polar vortex. In the vortex, the removal of NO, NO_2, and HCl, and the large enhancements of ClO appear to be triggered by formation of PSCs.

• Enhanced sulfate loading from Mt. Pinatubo may affect regions of the atmosphere where the fractional conversion resulting from pre-Pinatubo aerosol loading is incomplete, which is increasingly true at lower latitudes and at altitudes above 20 km. Column amounts of NO_2 were observed by the DC-8 to be notably depressed at mid-latitudes this year, as compared to past years. Ozone levels were reduced within the Pinatubo aerosol layers in the tropics.

Mission Results

Results from this mission are presented in a question and answer format and are drawn from observational data, diagnostic calculations, and an extensive analysis of the region's meteorology. Four sections address, in order: the approach to quantifying ozone loss, mission results obtained at arctic latitudes, issues surrounding the thinning of ozone at mid latitudes, and finally, the process used to establish the conclusions cited in this briefing.

General Approach

(1) How did this mission seek to determine and understand ozone losses?

The natural abundance of ozone varies with altitude, latitude, and season, reflecting patterns in chemical production and loss, and dynamical transport of ozone. Measurements of O_3 alone are not sufficient to define the degree of chemical destruction within a specific region. This is particularly true in the middle and high latitudes of the northern hemisphere, where the natural variability of ozone is very large. Hence, this mission has utilized four complementary approaches for diagnosing ozone loss:

Simultaneous, in situ observations of ozone, winds and atmospheric chemical tracers (N_2O, CFC-11, CH_4), combined with global maps from the NOAA National Meteorological Center (NMC) of stratospheric circulation patterns along with computed dynamical tracers and air parcel trajectories. The *in situ* observations and global analyses provide the information to define the atmospheric motion. Research over the past five years has demonstrated the importance of placing ozone observations in an analytical framework, whereby ozone changes resulting from atmospheric motion can be differentiated from chemical loss.

Observations of chemical species both directly responsible for ozone destruction in the stratosphere (ClO, BrO, and NO_2), and indirectly responsible (HCl, $ClONO_2$, $HONO_2$, H_2O, total reactive nitrogen) through linking chemical reactions. Studies in the Antarctic have shown that ClO and BrO concentrations determine the rate of catalytic ozone loss within the airmass in

which they are measured. Laboratory studies provide fundamental data defining chemical reaction rates, absorption cross-sections, and molecular structures.

Global maps of total ozone by the Total Ozone Mapping Spectrometer (TOMS) on board the Nimbus-7 satellite. A comparison of measurements taken during this mission with established historical values of ozone developed for the northern hemisphere over the 13-year lifetime of TOMS provides insight into the global distribution of ozone change.

Vertical cross sections of ozone and aerosols from the Differential Absorption Lidar (DIAL) aboard the DC-8 aircraft. The aircraft was used to search for regions inside the vortex with unusual vertical profiles of ozone that might suggest correlation between ozone loss and either the Pinatubo aerosol or polar stratospheric clouds (PSCs).

Arctic Latitudes

(2) What did the mission reveal concerning the chemical composition of the arctic lower stratosphere?

These studies, in conjunction with the AASE-I investigation of the arctic vortex in January and February of 1989, demonstrate that the conversion of inorganic chlorine (HCl and ClONO₂) to ClO does not require unusual conditions. We believe that ClO mixing ratios exceeding 1000 parts per trillion by volume (pptv) will emerge annually by mid-January throughout the lower stratospheric vortex, except during unusually warm years.

Through the course of twenty-five ER-2 flights and nineteen DC-8 flights, encompassing latitudes from the southern tropics to the pole, the seasonal evolution in concentration of the reactive radicals ClO, BrO, and NO, and of the less reactive chlorine reservoirs, HCl and $ClONO_2$, has been observed from the fall, prior to PSC formation, through winter to the beginning of spring.

The dramatic changes observed in the chlorine composition of the arctic lower stratosphere may be divided into three phases:

(i) Prior to and during the onset of PSCs: At high latitudes, ClO was in the range of 30-50 pptv in October and increased to 130 pptv (at northern latitudes) in mid-December. These values are significantly greater than expected, based on models that do not take proper account of reactions on aerosols. *In situ* measurements of HCl are lower than expected from model calculations (even those with aerosol reactions) throughout the period.

(ii) Winter occurrence of PSCs: After the onset of PSC temperatures, ClO increased to 500 pptv in the vortex in mid-December. Conversion of inorganic chlorine to ClO was observed inside the vortex by the ER-2 in December, 1991, and January, 1992, as large losses in HCl (reductions of as much as 1000 pptv) occurring simultaneously with large increases in ClO. In early January, ClO levels regularly approached 1000 pptv, increasing to 1500 pptv by the third week. These ClO levels represent a large fraction of the available inorganic chlorine in the stratosphere and are the highest values observed by the ER-2 in either hemisphere. Using back trajectory analysis, air parcels with low levels of HCl and high levels of ClO were found to have experienced temperatures at or below those required for PSC formation within a few days prior to sampling. Conversely, air parcels showing no evidence of chlorine conversion had not recently experienced PSC formation temperatures. Column measurements of HCl and $ClONO_2$ from the DC-8 were low inside the vortex, with a maximum $ClONO_2$ amount at the edge of the vortex in January. In January and February,

1992, there was little evidence for the irreversible removal of total reactive nitrogen, NO_y = HNO_3 + N_2O_5 + NO_3 + NO_2 + NO.

(iii) Disappearance of PSCs: Following a minor warming event in late January, temperatures rose above the PSC threshold and high ClO concentrations at ER-2 altitudes began to decline just inside the vortex, approaching 1000 pptv by mid February, and dropping to 200 pptv by late March. With the decrease in ClO after the cessation of PSCs, HCl and $ClONO_2$ were observed to increase, the latter more rapidly. The springtime decline of ClO and the resulting formation of $ClONO_2$ arises from the increased production of NO_2 from nitric acid released from PSCs as sunlight returns.

Concentrations of BrO between 4 and 8 pptv, accounting for 20-40% of the total inorganic bromine, were observed. These concentrations were not significantly affected by the occurrence of PSCs, nor did they vary significantly throughout the period of observation.

In situ observations of NO were combined with those of ozone and ClO to estimate NO_x (= NO + NO_2) in sampled air parcels. The value of NO_x/NO_y is used as an index of partitioning within the NO_y reservoir. Throughout the mission, when ClO levels were elevated, NO_x/NO_y values were suppressed at high latitudes. The depletion of NO and NO_2 within the NO_y reservoir is consistent with low photolysis rates of nitric acid at high latitudes in conjunction with the conversion of NO_x to nitric acid, via surface reactions on aerosols.

(3) What is the evidence for ozone loss in the Arctic?

Ozone loss was analyzed in the vortex for altitudes below 20 km. Calculations based on the observed time evolution of ClO, BrO, HCl, $ClONO_2$,, NO and NO_2 in the vortex in January and February predict ozone losses of approximately 20% between 15 and 20 km, consistent with observed ozone and tracer data obtained by the aircraft. The magnitude of total ozone loss was limited by the brevity and timing of the period during which temperatures remained below the PSC threshold (-78°C). These losses are quite significant but should not be described as an ozone hole.

Historical observations of the seasonal cycle in polar ozone indicate that from October through March, descent of ozone-rich air in the vortex substantially increases ozone in the lower polar stratosphere, particularly in the 15-20 km region. Changes in ozone at a particular altitude represent a balance between: (a) increases resulting from an influx of ozone from lower latitudes and higher altitudes, and (b) losses due to chemical destruction. Observations of ozone, referenced to both the H_2O and CFC-11 tracer fields, indicate net local decreases of ozone of about 20% in the 16-17 km range, while the balance at higher altitudes results in a small net increase in ozone. Although these results are preliminary, they are consistent with model calculations and with the DC-8 observations between 15 and 18 km.

Simultaneous observations of O_3, ClO, BrO and total reactive nitrogen (NO_y) in the antarctic vortex during the period of rapid ozone erosion in 1987 established the relationship between chlorine monoxide and bromine monoxide concentrations and the rate of ozone loss. The AASE-II series of ER-2 flights detailed the time evolution of ClO and BrO concentrations within the arctic vortex from early January through mid-March. Using ozone destruction rates derived from antarctic analysis, calculations based on AASE-II data predict ozone losses of approximately 20% between 15 and 20 km altitude, consistent with observations. The amount of ozone lost from the total column depends upon the vertical extent of the amplified ClO/BrO concentrations. Calculations suggest that the total ozone column decreases by approximately half the percentage change that occurs between 15 and 20 km. Calculations guided by the simultaneous observation of ClO, BrO, HCl, $ClONO_2$, NO and NO_2 during January through March also predict that more

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ozone loss would have occurred if the period over which temperatures remained below the PSC threshold (-78°C) extended well into February, as they have in approximately half of the last ten years.

(4) How did the meteorological conditions of the 1991/92 Arctic vortex compare with those of previous years?

Global meteorological analyses show that the period of cold temperatures (specifically, temperatures below the nitric acid trihydrate (NAT) phase transition at -78 °C, allowing PSC formation) was significantly shorter than normal at and below ER-2 cruise altitude.

Temperatures obtained from the NOAA National Meteorological Center were used to determine the climatology of the northern hemisphere. As during most northern winters, stratospheric temperatures in 1991/92 were cold enough for formation of PSCs but were not cold enough for extensive water ice particle formation. During a 39-day period from mid-December to mid-January, temperatures were intermittently low enough to form PSCs at the 20 km level. A minor stratospheric warming in mid-January raised temperatures above the PSC limit. This 39-day period contrasts with a 79-day period in 1988/89, and a 68-day range during an average winter.

The stratospheric polar vortex developed in early fall and reached maximum intensity in mid-winter. The 1991/92 polar vortex was not unusually strong, but did persist for an unusually long period (early April). The years 85/86, 87/88, 89/90, and 91/92 were each characterized by a persistent polar vortex.

(5) Did the presence of Mt. Pinatubo aerosol have significant impact on the chemical composition of the polar vortex?

The abundance of reactive chlorine in the Arctic vortex was dominated by reactions occurring on PSCs, rather than by reactions on either volcanic or background sulfate aerosols.

The high abundances of ClO (in excess of 500 pptv) are linked to the advent of PSCs. Trajectory studies (the tracing of airmass motion backward in time from the point of observation by the ER-2) reveal that airmasses characterized by (i) very high concentration of ClO, (ii) nearly complete removal of HCl, and (iii) changes in the particle size distribution, were several days earlier within regions characterized by temperatures below the PSC formation threshold. Trajectory analyses of immediately adjoining airmasses that showed no such perturbations in ClO, HCl, or particle size distribution indicated that these airmasses were not within regions with temperatures below the PSC formation threshold. While we believe that reactions on liquid aerosols are important, conversion of inorganic chlorine (HCl and $ClONO_2$) to ClO on PSCs is substantially faster, masking any reactions on background aerosols. This conclusion holds even for surface area enhancements of a factor of 30, characteristic of the Mt. Pinatubo cloud.

Lidar observations from the DC-8 showed that the Pinatubo aerosols were concentrated at and below the typical ER-2 flight altitudes inside most of the vortex. The ER-2 encountered the main aerosol layer from Pinatubo at the lowest altitudes in the descent profiles within the vortex. Pinatubo aerosols at high altitudes (up to 26 km) did not reach northern high latitudes soon enough to be entrained within the vortex upon its formation in early winter.

Air outside of the vortex was observed by the DC-8 instruments to move through cold regions, in which both NAT and ice clouds were forming. This air, with only brief exposure time to PSCs, was highly depleted in $HONO_2$, $ClONO_2$, and HCl. Air that had moved only through warmer regions of the Pinatubo cloud exhibited near-normal mid-latitude abundances of $HONO_2$, $ClONO_2$,

and HCl. These observations not only show that PSCs are more important for processing the air than are warm volcanic clouds, but also that a single rather brief exposure to PSCs is capable of significantly processing the air.

(6) Are future arctic ozone losses likely?

Analysis of results from both arctic airborne missions, AASE-I in 1989 and AASE-II in 1991/92, have isolated two key variables that determine the amount of ozone destroyed in any given year. The first is the amount of chlorine and bromine present in the stratosphere. The second is the timing and vertical extent over which temperatures in the vortex remain below the PSC threshold (-78°C).

The two AASE missions have demonstrated that a large fraction of all inorganic chlorine (HCl and $ClONO_2$) in the stratosphere is converted to ClO and its dimer whenever the temperature in a particular region of the vortex reaches the PSC threshold (-78°C). Therefore, the concentration of reactive chlorine following PSC processing is proportional to total chlorine loading. Additionally, in the absence of NO_x, reactive bromine is proportional to the bromine loading. Knowledge of the ClO and BrO concentrations within the vortex allows the determination of the rate of ozone loss.

These missions in conjunction with the antarctic mission in 1987 have further demonstrated that the total amount of ozone lost in the vortex in any given year (for which the total chlorine and bromine loading are specified) depends foremost on the timing and vertical extent of temperatures within the vortex that remain below the PSC threshold (-78°C). The reason is at least twofold: (i) PSCs retain nitric acid, preventing the reintroduction of NO_2, which converts ClO back to the more stable form of chlorine, $ClONO_2$; and (ii) PSCs recycle HCl and $ClONO_2$ back into ClO. The amount of ozone removed is sensitive to the amount of NO_2 reintroduced because ClO is removed primarily by reaction with NO_2 to form $ClONO_2$. For example, at a current total chlorine loading of 3500 pptv, if vortex temperatures remain below PSC threshold until the fourth week of January, calculations consistent with observed levels of HCl, ClO, BrO, NO, NO_2, $ClONO_2$ and $HONO_2$ predict that approximately 20% of the ozone will be destroyed by the chlorine and bromine cycles at ER-2 altitudes. The impact on total column ozone depends upon the vertical extent of the cold region and for typical temperature profiles ranges from one quarter to one half the fractional loss at ER-2 altitudes. If in future years temperatures remain below PSC threshold until the fourth week of February, a circumstance that has occurred a number of times in the last decade, ozone loss will increase substantially.

Mid Latitudes

(7) What did the mission reveal concerning the chemical composition of the mid-latitude stratosphere?

The mission revealed strong evidence for the influence of sulfate aerosols on stratospheric chemistry from several new, independent sets of measurements. These include:

ClO abundances near 20 km that are a few times larger than gas-phase chemical model predictions but in broad agreement with models including surface reactions of N_2O_5 on sulfate aerosols.

Observations that NO concentrations are many times smaller than gas-phase chemical model predictions, again in broad agreement with models including surface reactions on sulfate aerosols.

In addition to their absolute values, both the seasonal and latitudinal variations observed in ClO and NO conflict with gas-phase model predictions but are consistent with our understanding of the

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impact of sulfate aerosols. In particular, the ClO increased substantially from summer to winter, in direct contradiction to gas-phase chemistry.

Observations of NO_2 column abundances that are significantly lower than those obtained in 1989 under comparable conditions. This suggests important effects from the added sulfate aerosols present in the stratosphere this year due to the eruption of Mt. Pinatubo, notably an increased altitude range over which heterogeneous processes convert NO_2 to nitric acid and a resulting increase in ClO.

The mission also provided important information on the abundances, trends, and origin of stratospheric chlorine, bromine, and fluorine.

Measurements of long-lived tracers show that the total chlorine and total bromine entering the tropical lower stratosphere is about 3.5 ppbv and 20 pptv, respectively, of which 2.9 ppbv of chlorine and about 8 pptv of bromine are manmade. In addition, column measurements of HF and HCl, made in 1989 and 1991, suggest that stratospheric fluorine and chlorine have been increasing by about 10% and 5% per year, respectively, consistent with releases of manmade compounds.

(8) What does the Total Ozone Mapping Spectrometer (TOMS) show with respect to this year's ozone distribution?

During 1992, TOMS measurements show that the hemispheric ozone average during January, February and most of March was lower than any previous year in the TOMS record. TOMS measurements also showed that total ozone values in the mid-latitude maximum were 10-15% lower than any previous year in the TOMS record. The mechanisms responsible for this situation are currently under study.

The Total Ozone Mapping Spectrometer (TOMS) instrument aboard the Nimbus 7 satellite has collected more than 13 years of total column ozone data, beginning in November 1978. TOMS data have been vital for the monitoring of the Antarctic ozone hole and more recently for quantifying changes in the ozone layer in the northern hemisphere.

Usually there is a substantial build-up of total column ozone in northern mid latitudes during the late winter and early spring. TOMS measurements show that this build-up of high total ozone values was unusually weak this winter. Specifically, total ozone values in the northern mid-latitude maximum were 10-15% lower compared to previous years. The mechanisms responsible for this reduction in ozone are currently under study.

To date in 1992, TOMS measurements show that the hemispheric ozone averages were as low or lower than any previous year in the TOMS record. However, the very lowest values of total ozone were similar to those found in previous years.

(9) To what extent do the results of this mission contribute to our understanding of the observed long-term decrease of mid-latitude ozone?

The results from this mission, particularly the observations of HCl, NO, NO_2, ClO, BrO and the tracers N_2O and CFC-11, support the conclusion, stated in the recent UNEP Report, that decreases in ozone are associated with increases in chlorine and bromine in the lower stratosphere.

Ozone changes at mid latitudes result from the combined influence of (i) chemical loss by chlorine, bromine, hydrogen and nitrogen catalytic cycles, and (ii) dynamical redistribution of ozone through the seasonal cycle. Observations of HCl, ClO, BrO, NO, NO_2 and the tracers N_2O and CFC-11 obtained during AASE-II have defined for the first time the relative importance with respect to ozone loss of the major nitrogen, chlorine and bromine cycles in the lower stratosphere

(15-20 km). These observations show that while a number of catalytic cycles contribute to the balance between ozone production and loss in the lower stratosphere, chlorine and bromine reactions have a significant and perhaps dominant role in the ozone loss budget. In addition, observed concentrations of NO, ClO and BrO highlight the critical importance of the bromine cycle to increasing ozone loss rates of ozone at mid latitude.

Models that are consistent with the simultaneously observed concentrations of HCl, ClO, BrO, NO, NO_2 and $ClONO_2$ predict long term ozone losses, primarily as a result of reactions involving ClO and BrO. These models are in general agreement with the observed ozone decrease at mid latitudes reported by ground-based and satellite data over the decade of the 1980s. It is important to note that major contributions to the balance between ozone chemical production/loss and dynamical redistribution through the seasonal cycle extend from 15 to 30 km and that the AASE-II results are focussed primarily on the altitude interval from 15 to 20 km.

(10) To what extent was the observed chemical composition in mid latitudes and the tropics influenced by the eruption of Mt. Pinatubo?

The eruption increased the natural abundances of sulfate particles, thereby potentially amplifying the effects of heterogeneous reactions. No evidence has been found for significant chlorine injections. At mid and high latitudes, the chemical perturbation that could be traced to Pinatubo was a suppressed mid-latitude NO_2 column concentration. Ozone levels in the tropics also were found to be reduced within the Pinatubo aerosol layers.

The TOMS instrument observed a stratospheric SO_2 injection from the eruption of Mt. Pinatubo which exceeded that measured or estimated from any other eruption in the past century. TOMS observed the SO_2 to decline quickly as it was converted to sulfuric acid particles. The optical depth (which is proportional to the column surface area of the particles) of the resulting global scale volcanic cloud was found by instruments on the DC-8 to be greater than that of the 1982 El Chichon eruption. The column surface area in the volcanic cloud exceeded the surface area of background aerosols by a factor of about 20 to 40 in the tropics and about 10 to 20 in the arctic vortex. DC-8 lidar measurements showed that the region of significantly enhanced surface area extended from the local tropopause up to about 26 km in the tropics, to about 22 km at northern mid latitudes, and to about 18 km in the arctic vortex. ER-2 observations showed that local surface areas were enhanced by factors of 20-30 at mid latitudes over non-volcanic levels. ER-2 and DC-8 particle analyses showed the volcanic cloud was dominated by submicron sized sulfuric acid particles.

Volcanic eruptions can potentially inject significant quantities of chlorine into the stratosphere. Measurements made in the Pinatubo cloud revealed that the eruption could have perturbed stratospheric chlorine levels by no more than about 5%, which is the equivalent of about one year's anthropogenic contribution to rising stratospheric inorganic chlorine levels. Although DC-8 column data do show a 5% yearly rise in inorganic chlorine over the past several years due to the anthropogenic contribution, no measurable contribution to stratospheric chlorine was observed in the dispersed Pinatubo cloud. Likewise, ER-2 measurements of HCl inside and outside of the volcanic cloud at mid latitudes did not show any evidence of enhanced stratospheric chlorine resulting from the Pinatubo eruption. No enhancement in stratospheric water vapor resulting from Mt. Pinatubo was observed.

Numerous theoretical studies have suggested the potential for volcanic eruptions to affect mid-latitude ozone levels. The proposed mechanism involves reactions occurring on the surface of sulfuric acid particles (which deplete NO_x). The depleted NO_x, in turn, would lead to an increase in ClO through gas phase chemical processes and the ClO would destroy ozone. The reactions depleting NO_x are very efficient even on the background stratospheric aerosols and therefore

stratospheric NO_x is not expected to decrease in direct proportion to increased aerosol loading. We found that NO_2 columns in the Arctic vortex, although low, were not lower than in 1989. At high latitudes outside the vortex the NO_2 column was slightly lower than in 1989. These results are in line with expectations that the volcanic cloud would have little impact on high latitude NO_x levels, which are already driven quite low by background sulfate aerosols. At mid latitudes, column NO_2 values were lower than in previous years, reflecting both (i) the increased altitude range over which heterogeneous conversion of NO_x to nitric acid took place within the volcanic cloud, and (ii) the higher concentrations of NO_2 (resulting from the faster photolysis rates of nitric acid) at lower latitudes that were thus sensitive to enhanced heterogeneous conversion to nitric acid on aerosol surfaces.

It is not clear whether the volcanic sulfate aerosol, which will be removed from the stratosphere by natural processes over the next few years, will increase the amount of mid-latitude ozone depletion that is expected to occur over this period due to rising inorganic chlorine levels from anthropogenic sources.

The DC-8 lidar measurements in the tropics showed a negative correlation between the presence of the Pinatubo aerosols and ozone levels compared to satellite climatology for that region. The maximum amount of the decrease was about 20% near the center of the Pinatubo layer at 23 km. These results agree with ozone changes across the Pinatubo layer found in ozonesonde data from the tropics.

(11) Have we learned anything new about the impact of aircraft exhaust on the stratosphere?

The importance of heterogeneous reactions on sulfate aerosols has been verified by these aircraft studies. Thus, the impact of additional NO_x on ozone in the lower stratosphere is expected to be much smaller than previously predicted and may now be closer to that simulated with the most recent global assessment models that include heterogeneous sulfate-layer chemistry.

Scientific Process

(12) What was the scientific process involved in coming to the above conclusions?

The above conclusions were based on a group synthesis of the viewpoints of more than 80 scientists involved in the AASE-II campaign. The observations and simulations involved in this mission have built upon a rich research heritage, including updated laboratory kinetic studies of gas and surface reactions. The ER-2 and DC-8 aircraft and many of the instruments have been involved in over a hundred stratospheric research flights. The methods and results are contained in numerous peer-reviewed journal publications including three special issues. The science team included both experimentalists and theorists, whose experience and background embraces chemistry and chemical modelling, physics, meteorology, and large-scale dynamics. In designing the mission and interpreting the data, the efforts of the principal investigators were augmented by an advisory and review group. The details of the results of the current campaign will be published in the peer-reviewed literature.
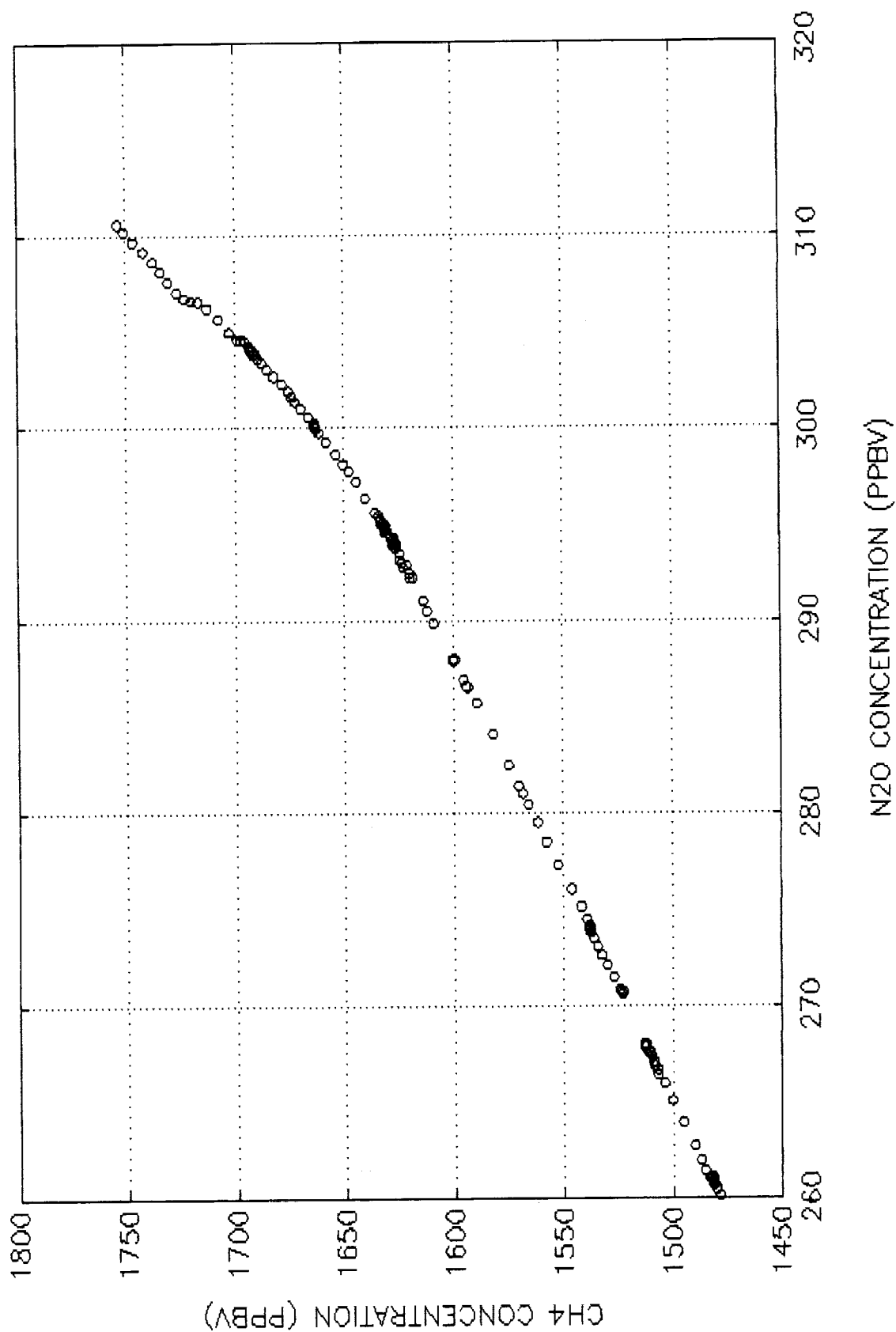
Figure 1a. Volume mixing ratio CH$_4$ as a function of N$_2$O mixing ratio for part of the DC-8 flight of 12 March 1992.
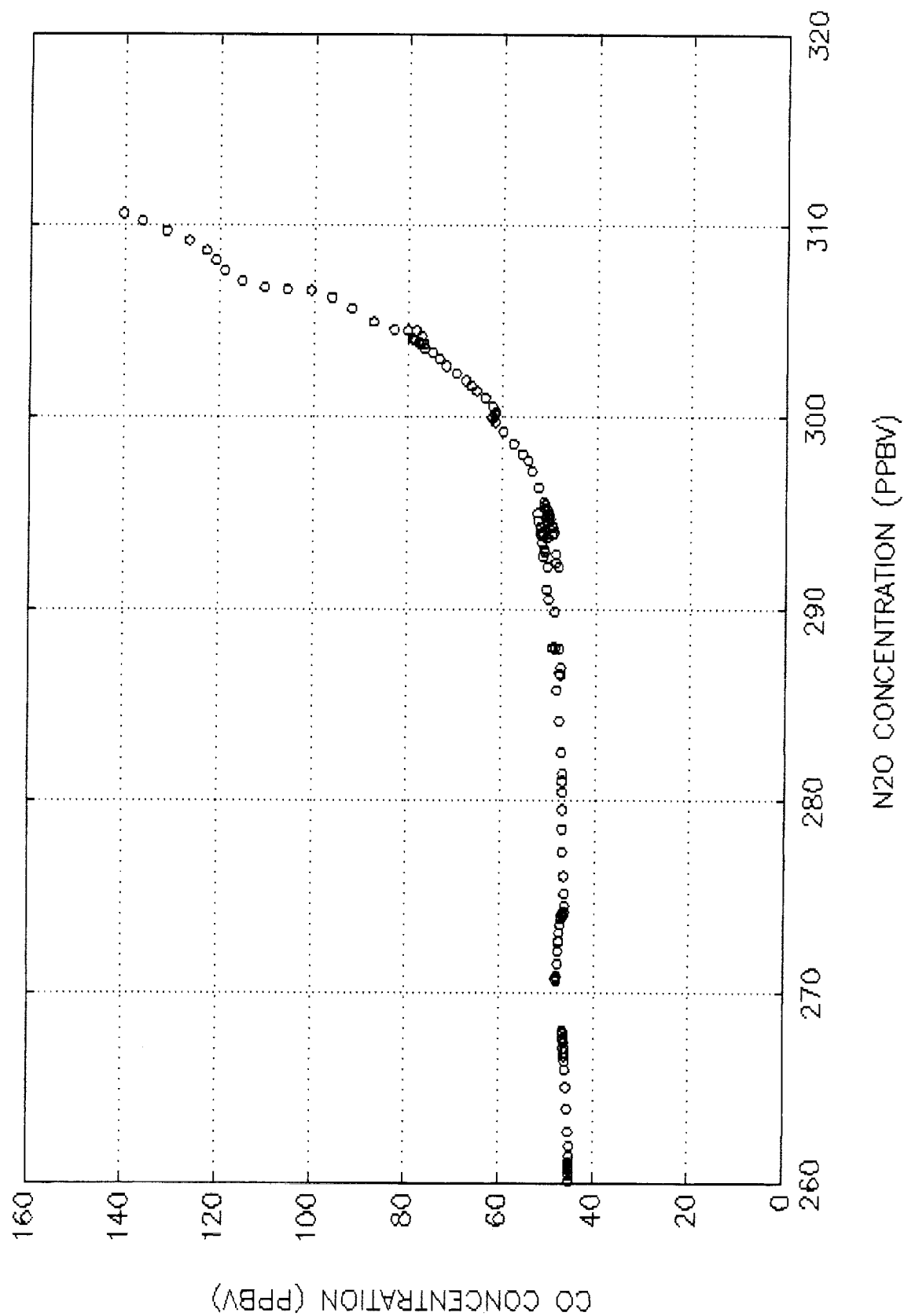
Figure 1b. Volume mixing ratio CO as a function of N_2O mixing ratio for part of the DC-8 flight of 12 March 1992.
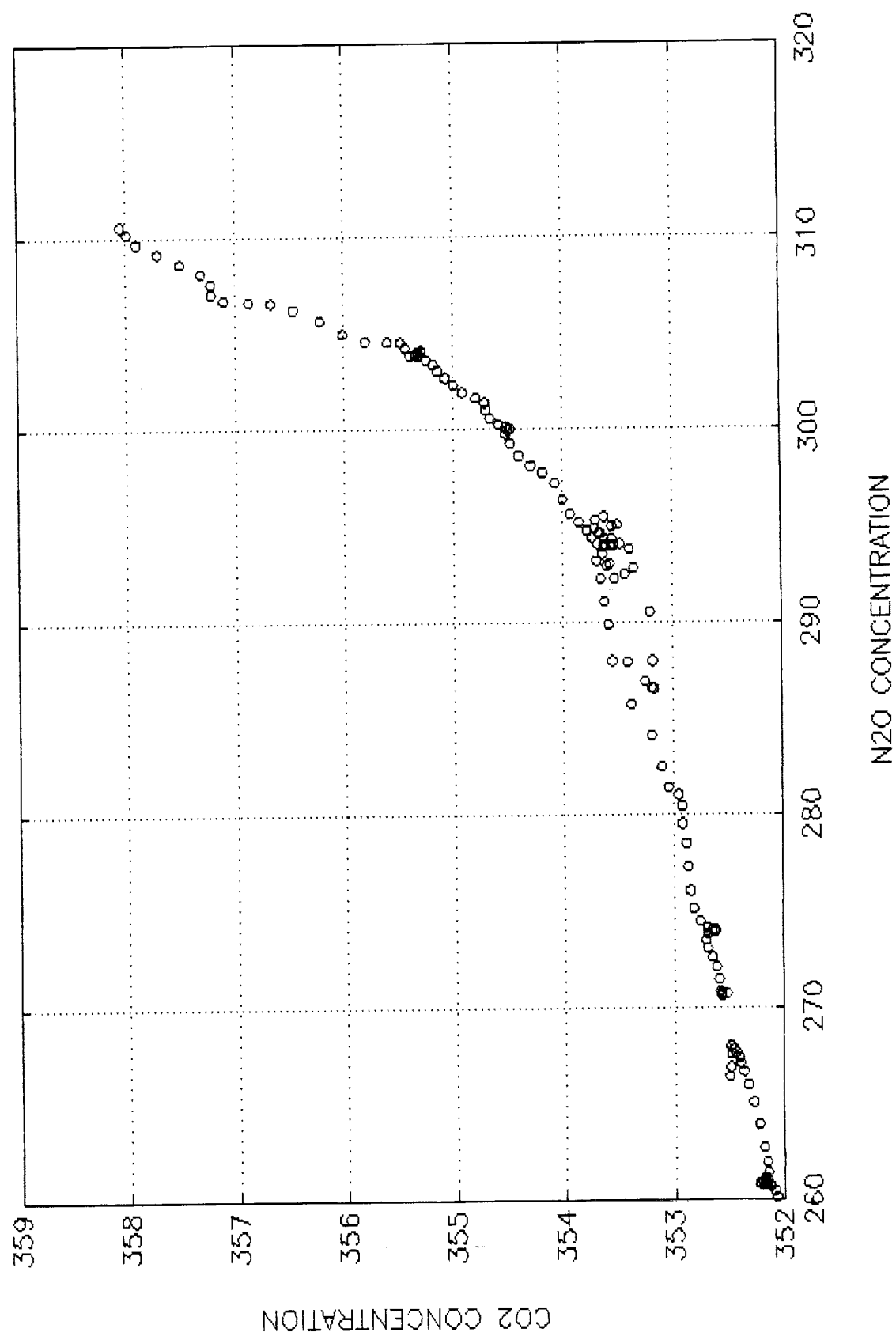
Figure 1c. Volume mixing ratio CO_2 as a function of N_2O mixing ratio for part of the DC-8 flight of 12 March 1992.
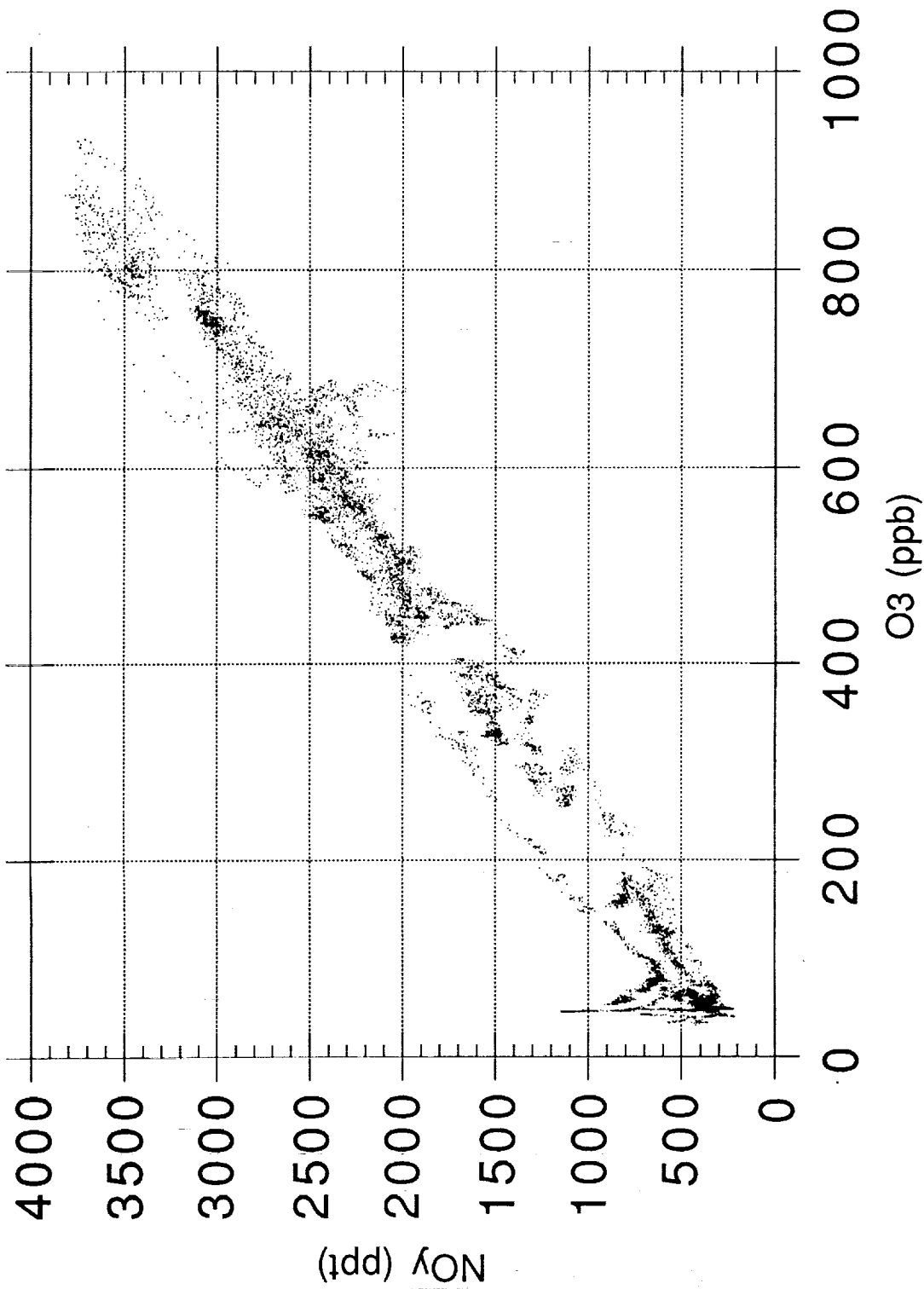
Figure 2. Volume mixing ratio NO_y as a function of O_3 mixing ratio for the DC-8 flight of 17 February 1992.

Mission 13
Descent into Bangor (43°N)
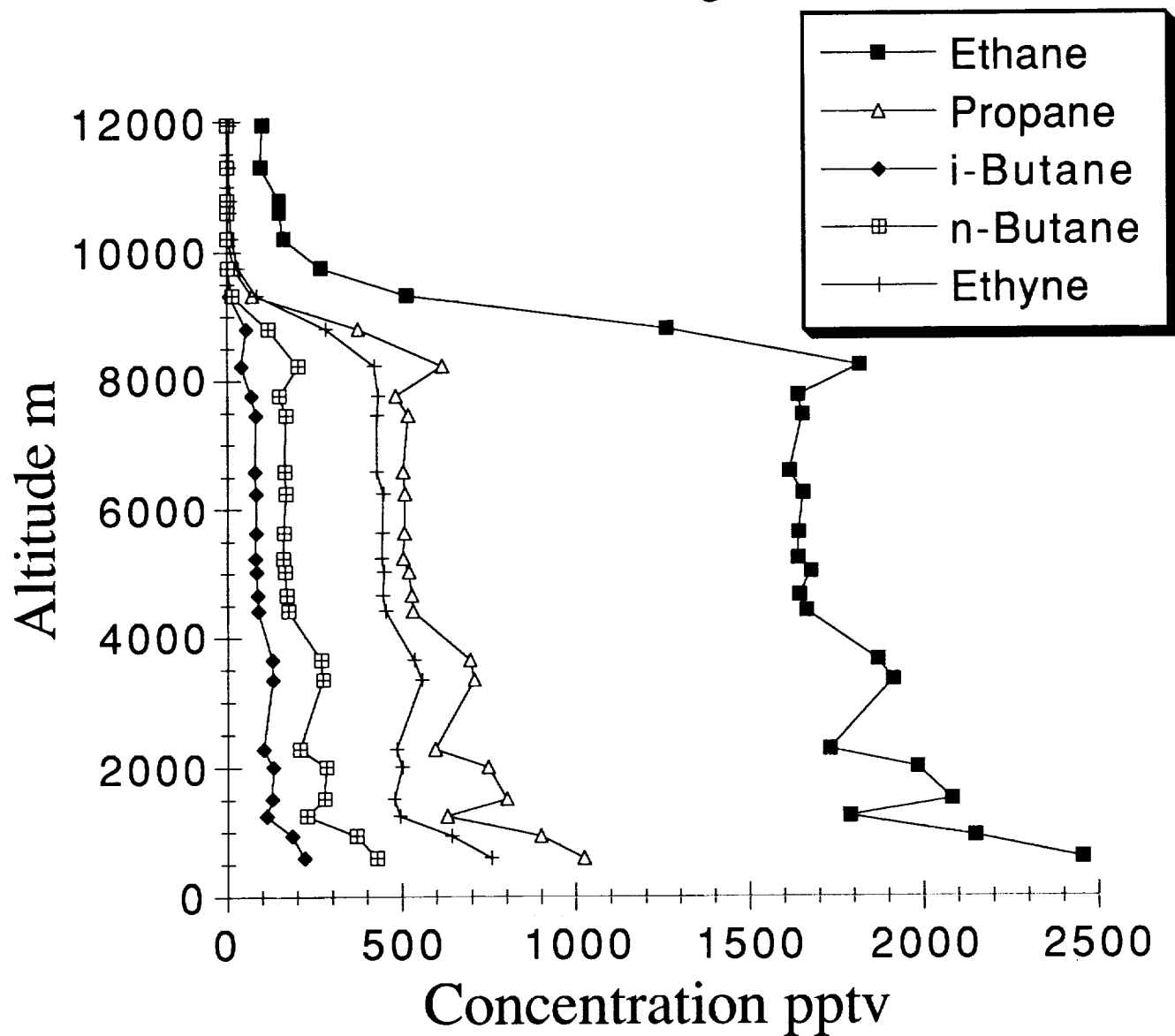
Figure 3a. Profiles of selected hydrocarbons during descent into Bangor, Maine, on the DC-8 flight of 20 February 1992.

Modified

Mission 13
Descent into Bangor (43°N)
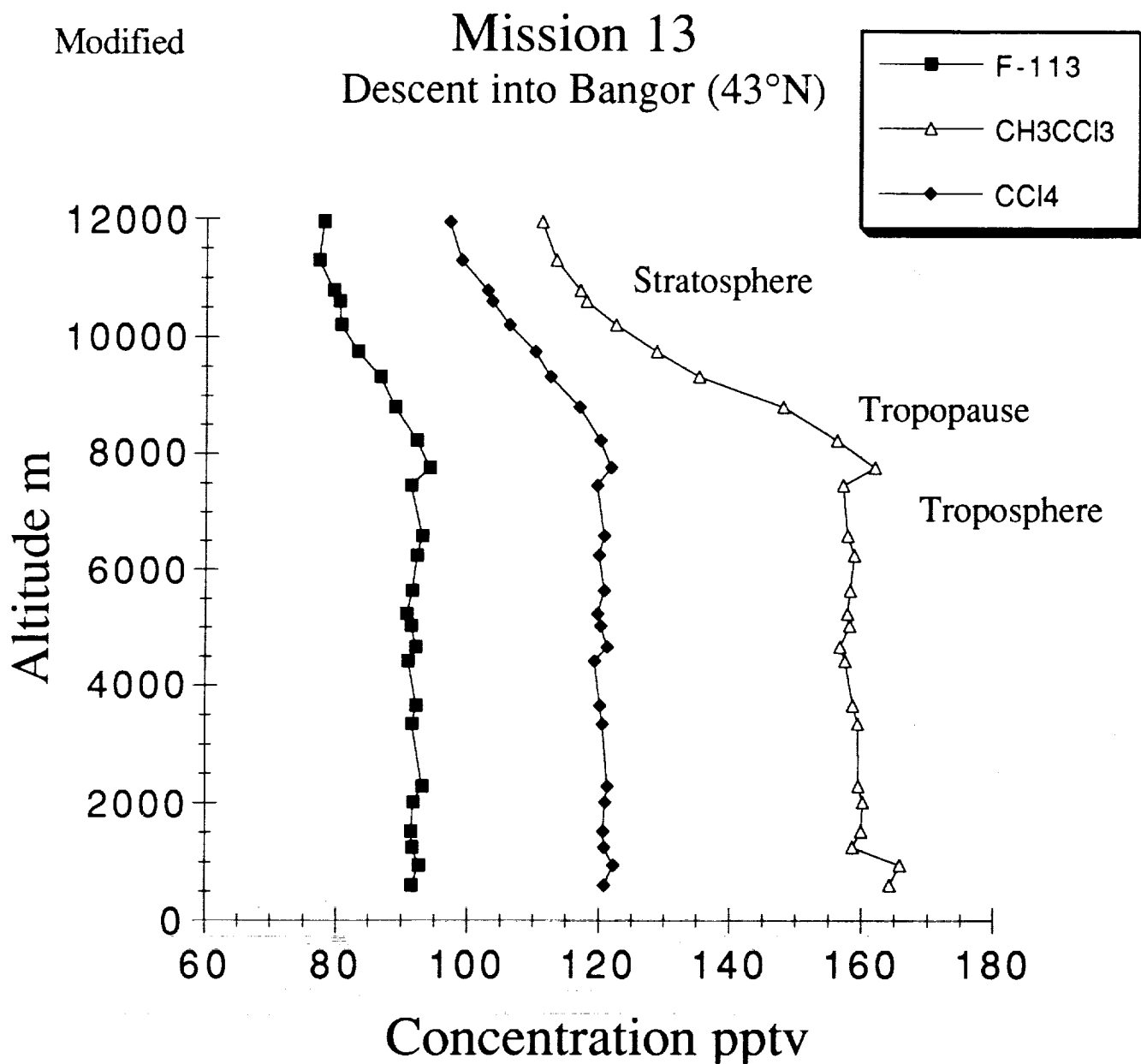
Figure 3b. Profiles of selected halocarbons during descent into Bangor, Maine, on the DC-8 flight of 20 February 1992.
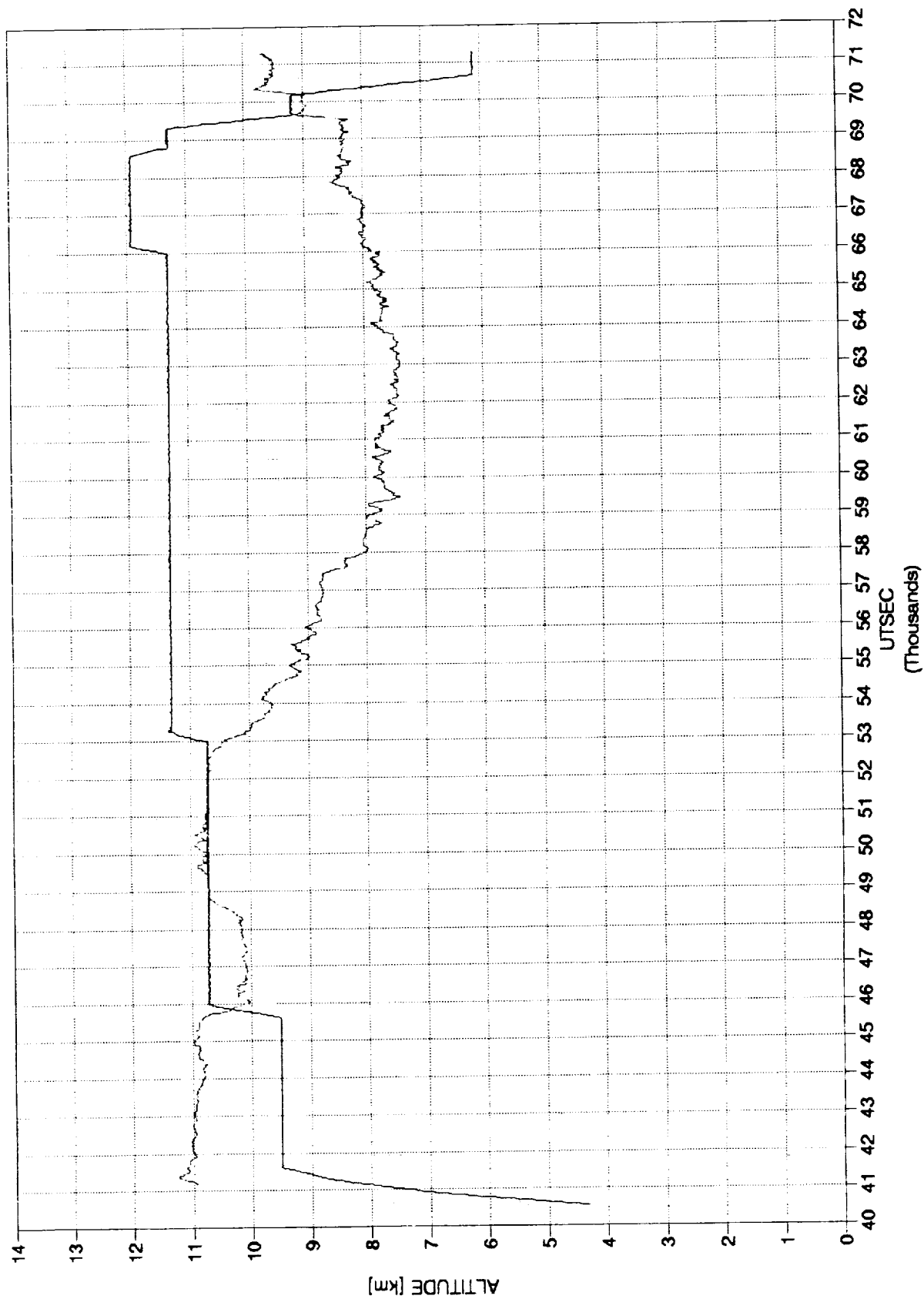
Figure 4. DC-8 flight level (solid line) and tropopause altitude (thin dotted line) determined by MTP for the flight of 17 February 1992.

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Polar Vortex: NOAA/CMDL/ACATS CFC Data and Harvard ClO
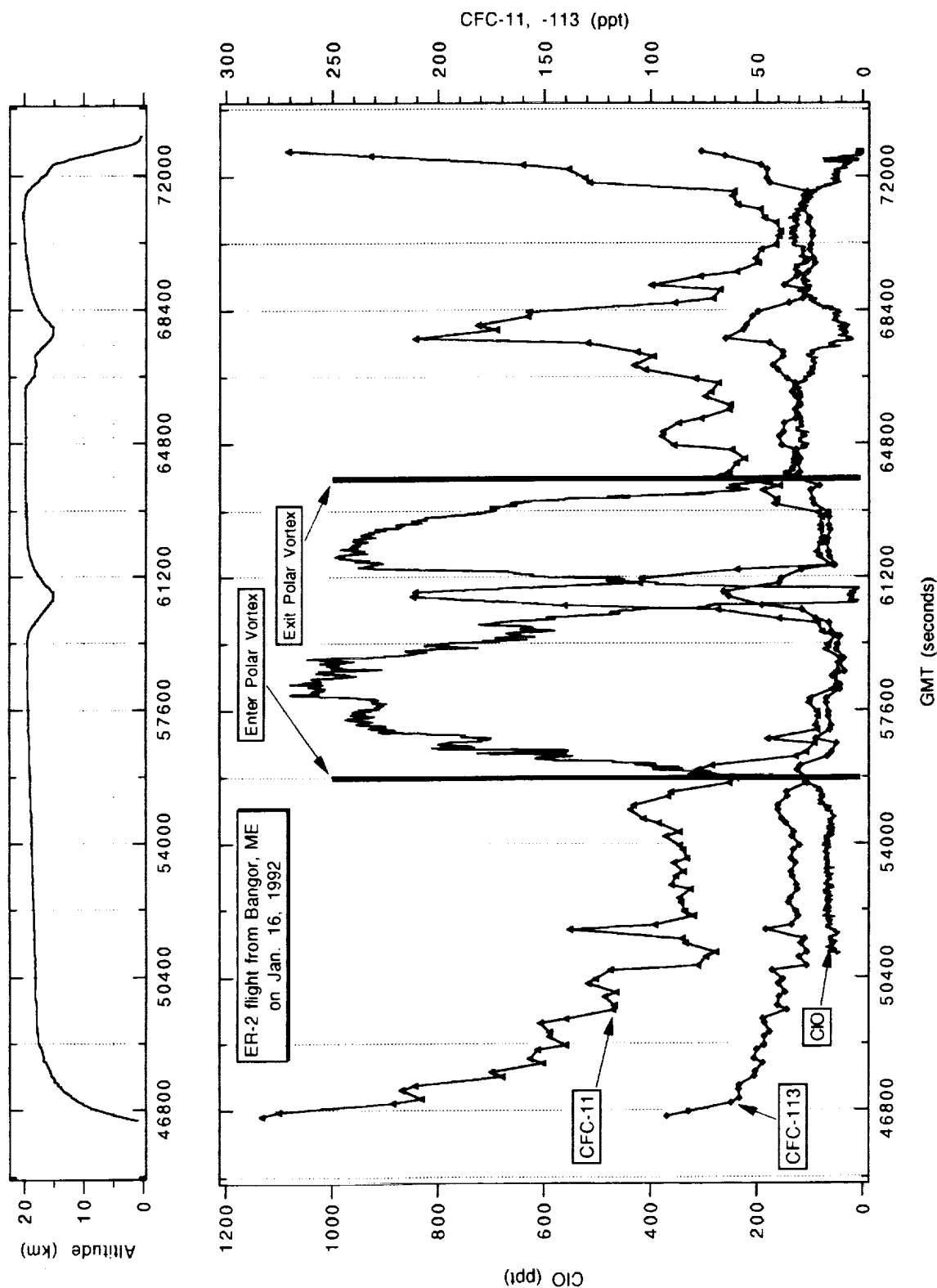
Figure 5a. Mixing ratios of CFC-11, CFC-113, and ClO on the ER-2 flight of 16 January 1992 through the polar vortex plotted as a function of time.
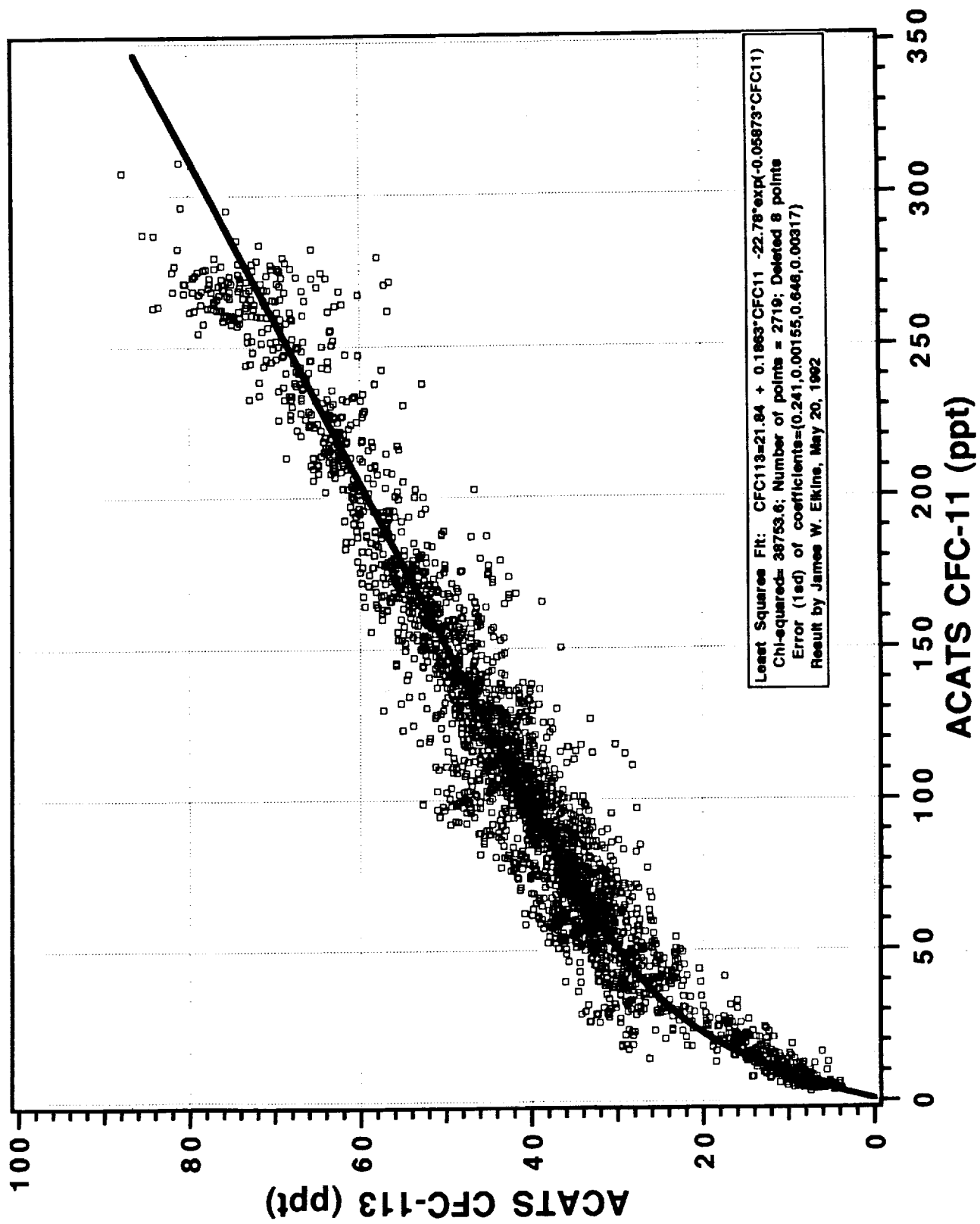
Figure 5b. Mixing ratios of CFC-11, CFC-113, and ClO on the ER-2 flight of 16 January 1992 through the polar vortex plotted as a scatter plot of CFC-11 versus CFC-113.
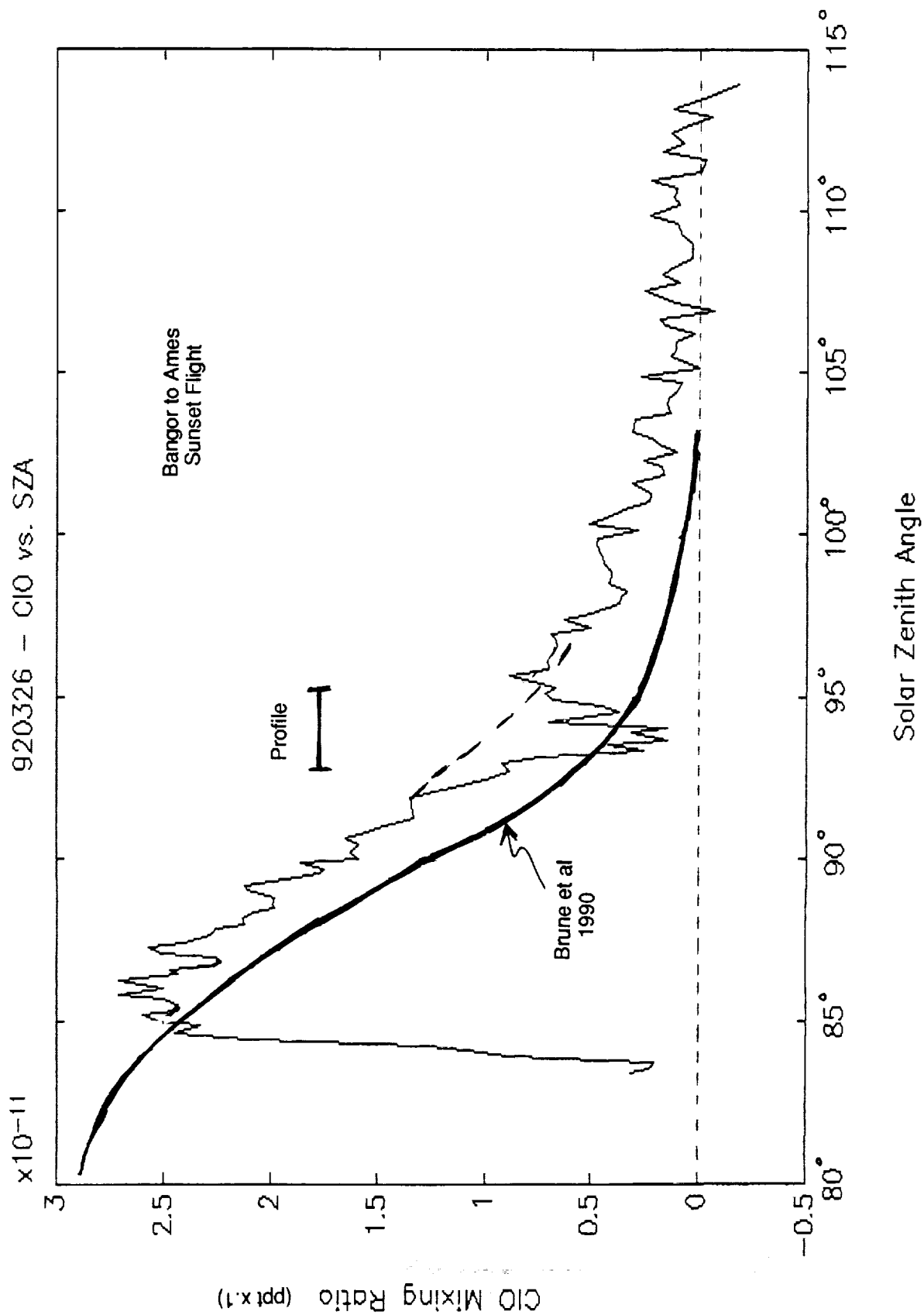
Figure 6a. ClO concentrations as a function of Solar Zenith Angle from the ER-2 flight of 26 March 1992 from Bangor to Ames during sunset (thin solid line); the period of the ER-2 dive is denoted "profile"; and a mean curve to the 1998 observations of Brune et al. are shown (thick solid curve).

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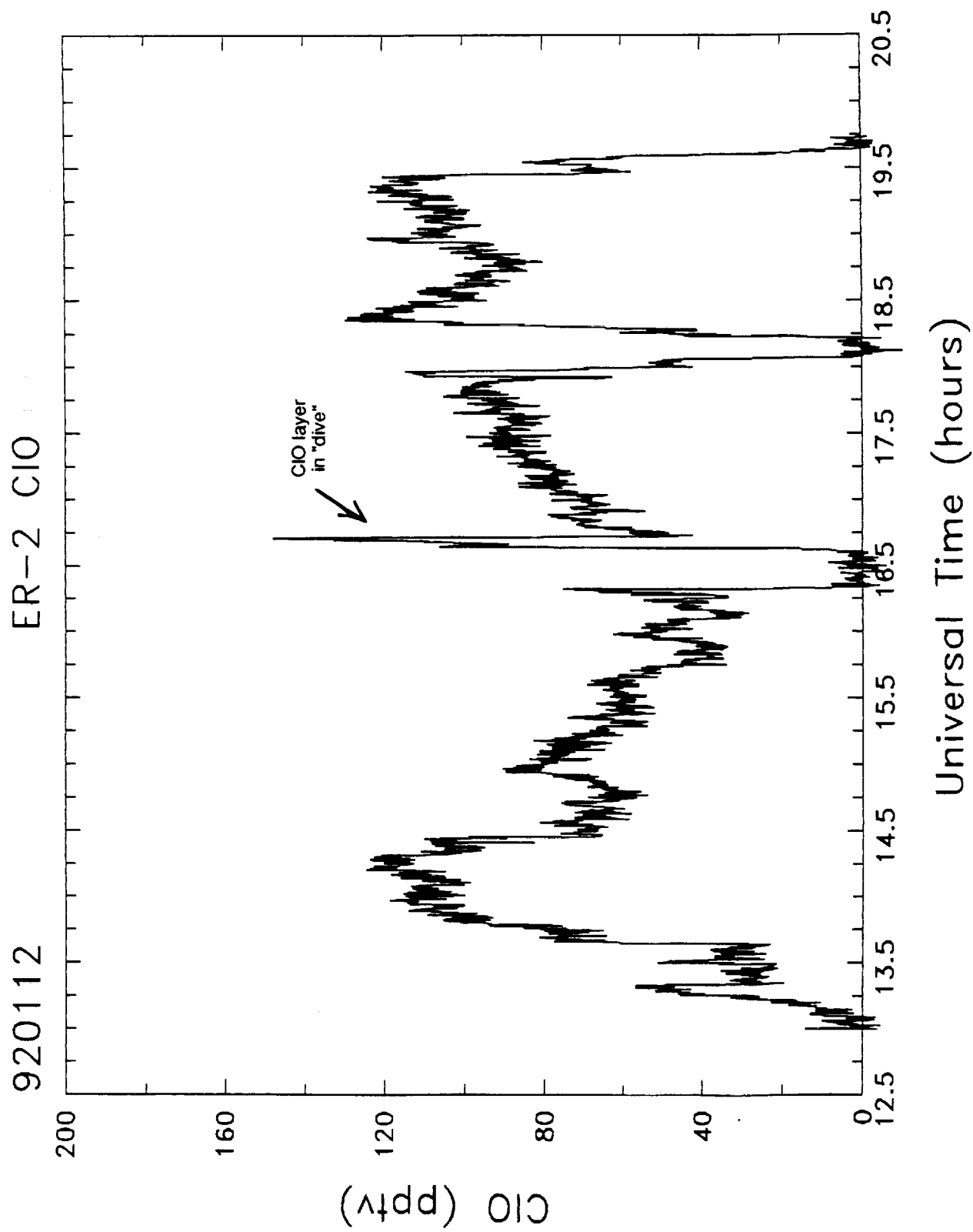
Figure 6b. Enhanced ClO concentrations during a dive on the flight of 12 January 1992.

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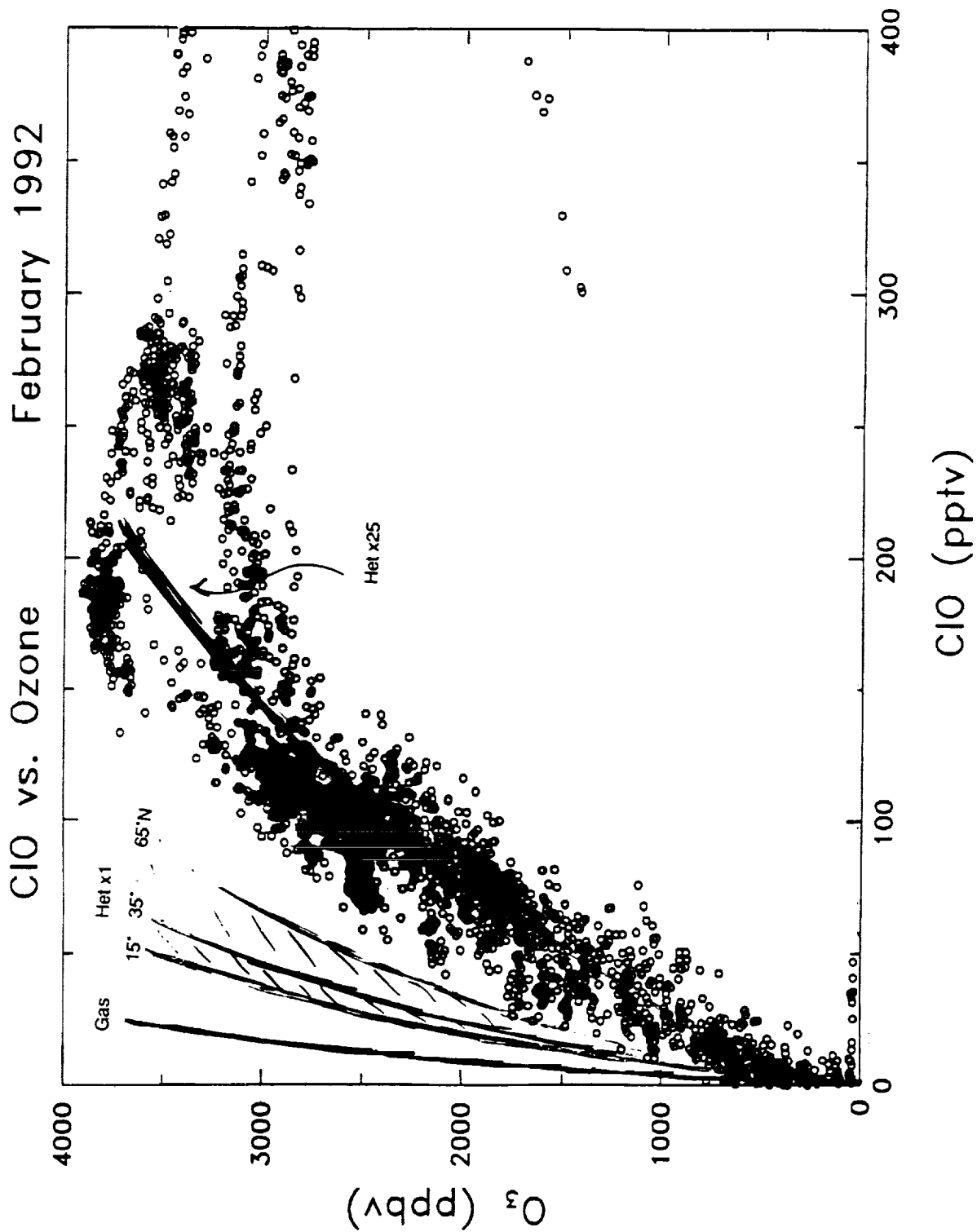
Figure 6c. CIO versus O_3 for a wide range of latitudes (20N - 70N) from the February flights (○); model predictions for gas-phase and heterogeneous chemistry at different latitudes are also shown; and calculations with 25 times background sulfate area goes through the measurement points.

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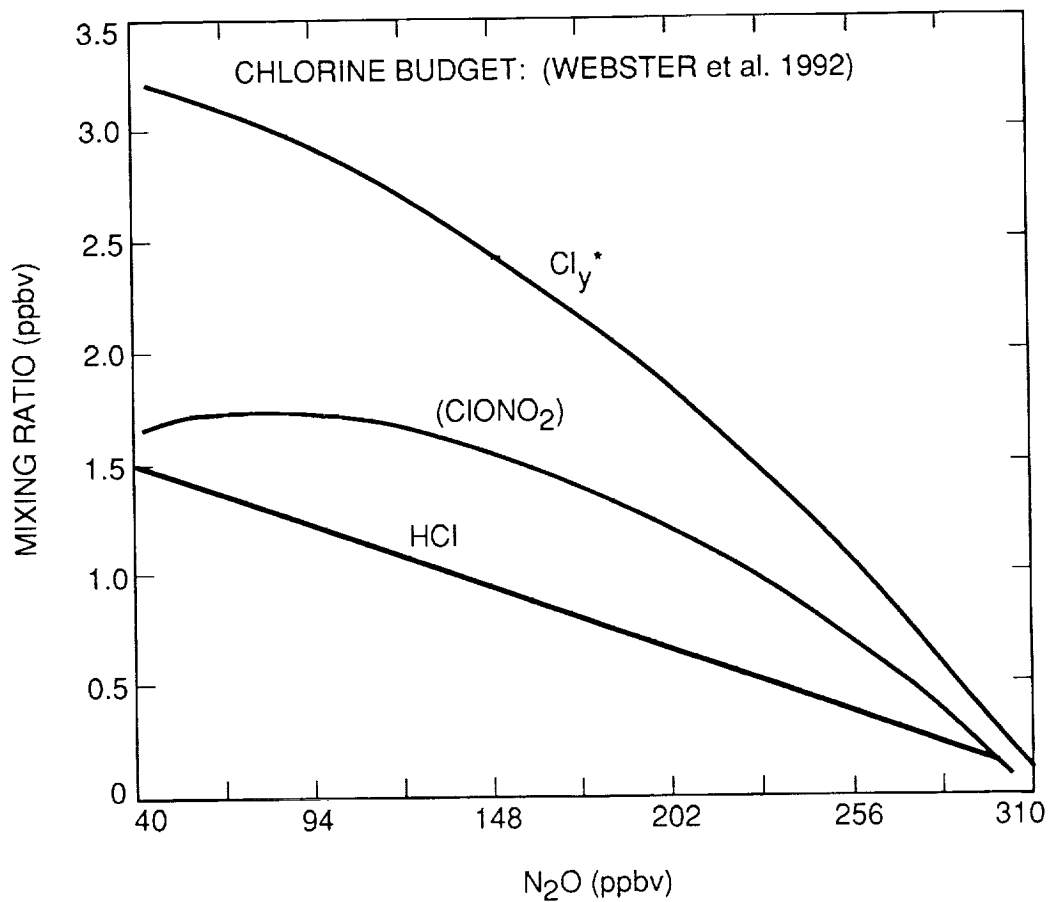
Figure 7. A linear fit of observed HCl versus N_2O is compared with the total expected inorganic chlorine abundance (Cl_y), also a function of N_2O. Model calculations of $ClONO_2$ are added on.
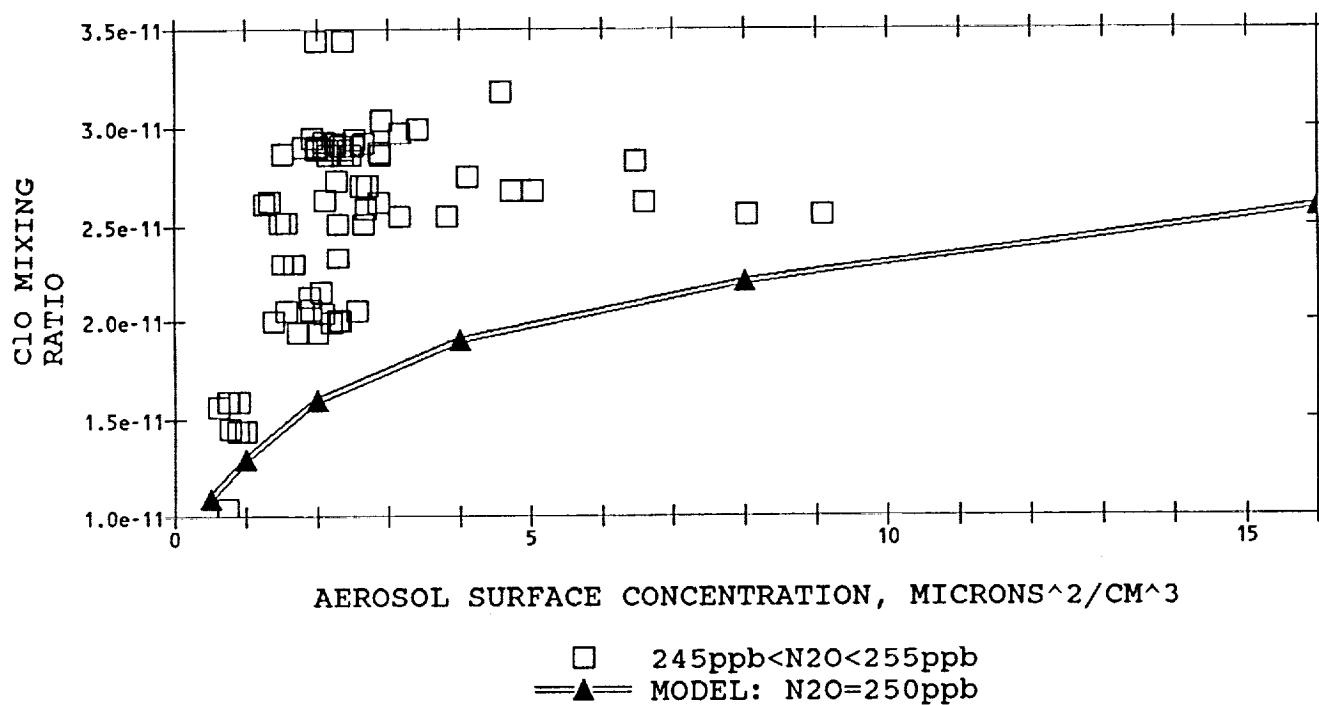
Figure 8. ClO mixing ratio versus aerosol surface area for the ER-2 flight of 17 September 1991. The measurements have been selected by N_2O abundance (245 to 255 ppb) and are compared with a chemical model. Aerosol surface was measured with the FCAS.

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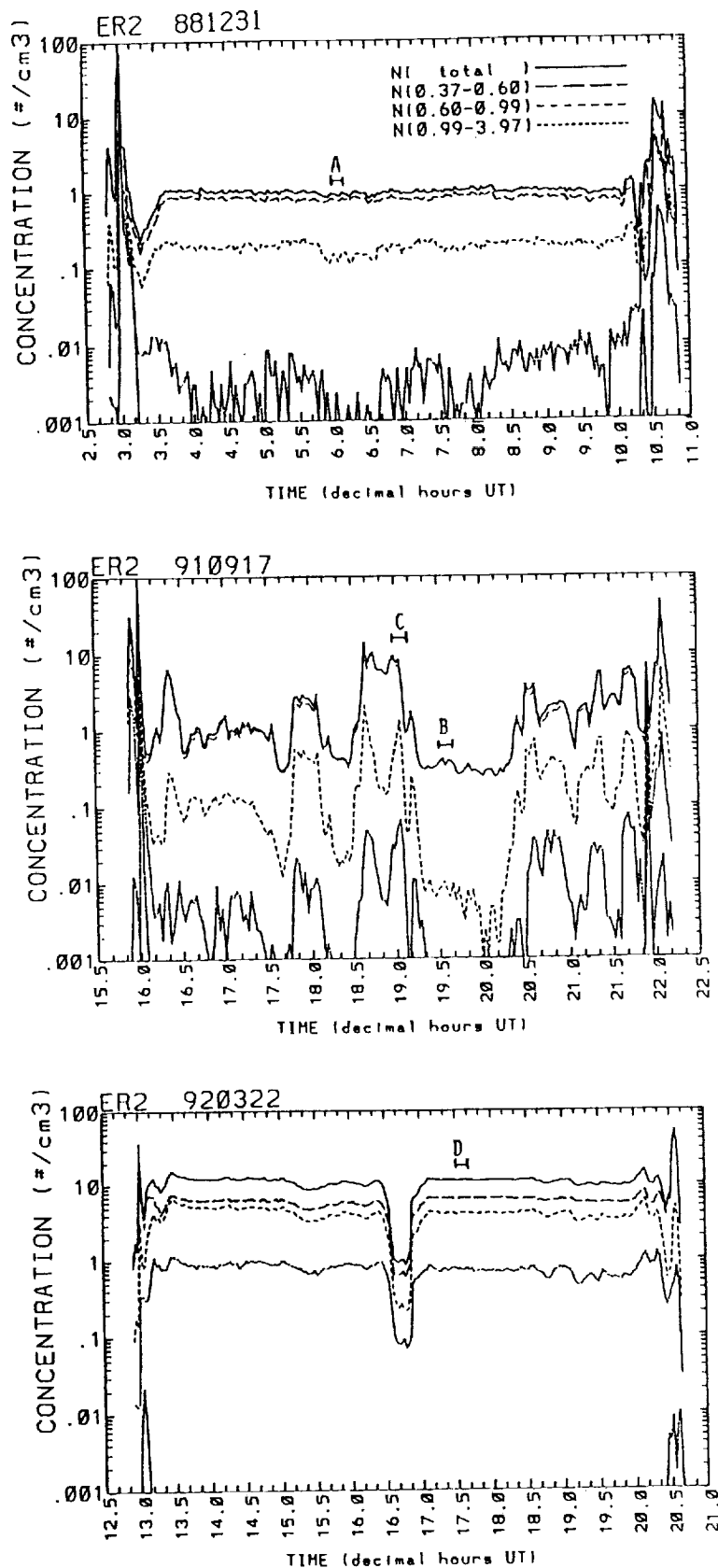
Figure 9. Aerosol measurements made by the FSSP 300 on the ER-2 during the flights of 881231, 910917, and 920322. Concentrations over different particle diameter intervals are as indicated in the legend. Total refers to the total concentration of particles > 0.4 microns.

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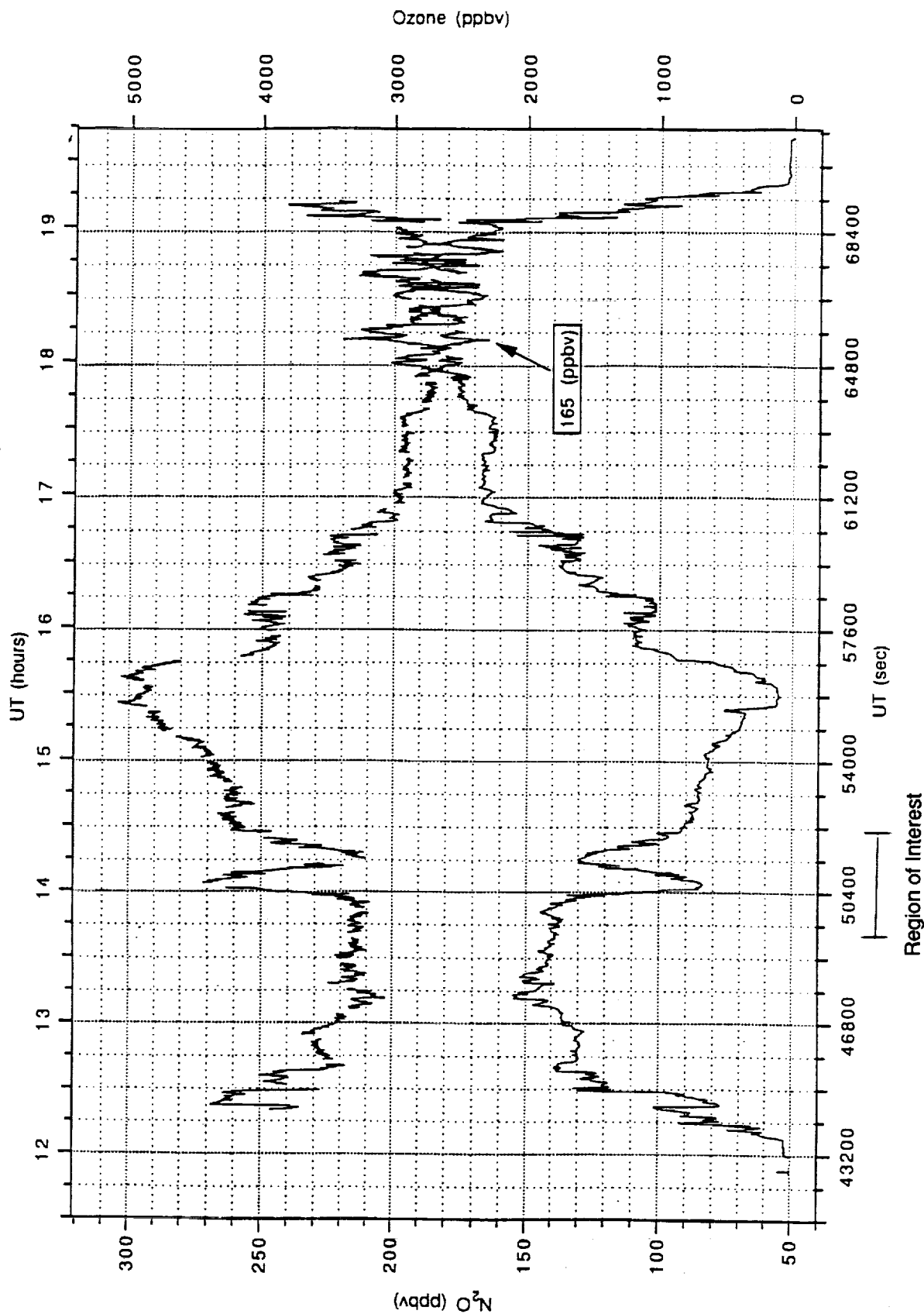
Figure 10.a Time line of N_2O (upper curve) and O_3 (lower curve) for the ER-2 flight of 22 February 1992 showing the simultaneous drop in N_2O and increase in O_3 at 1415 UT (hrs).
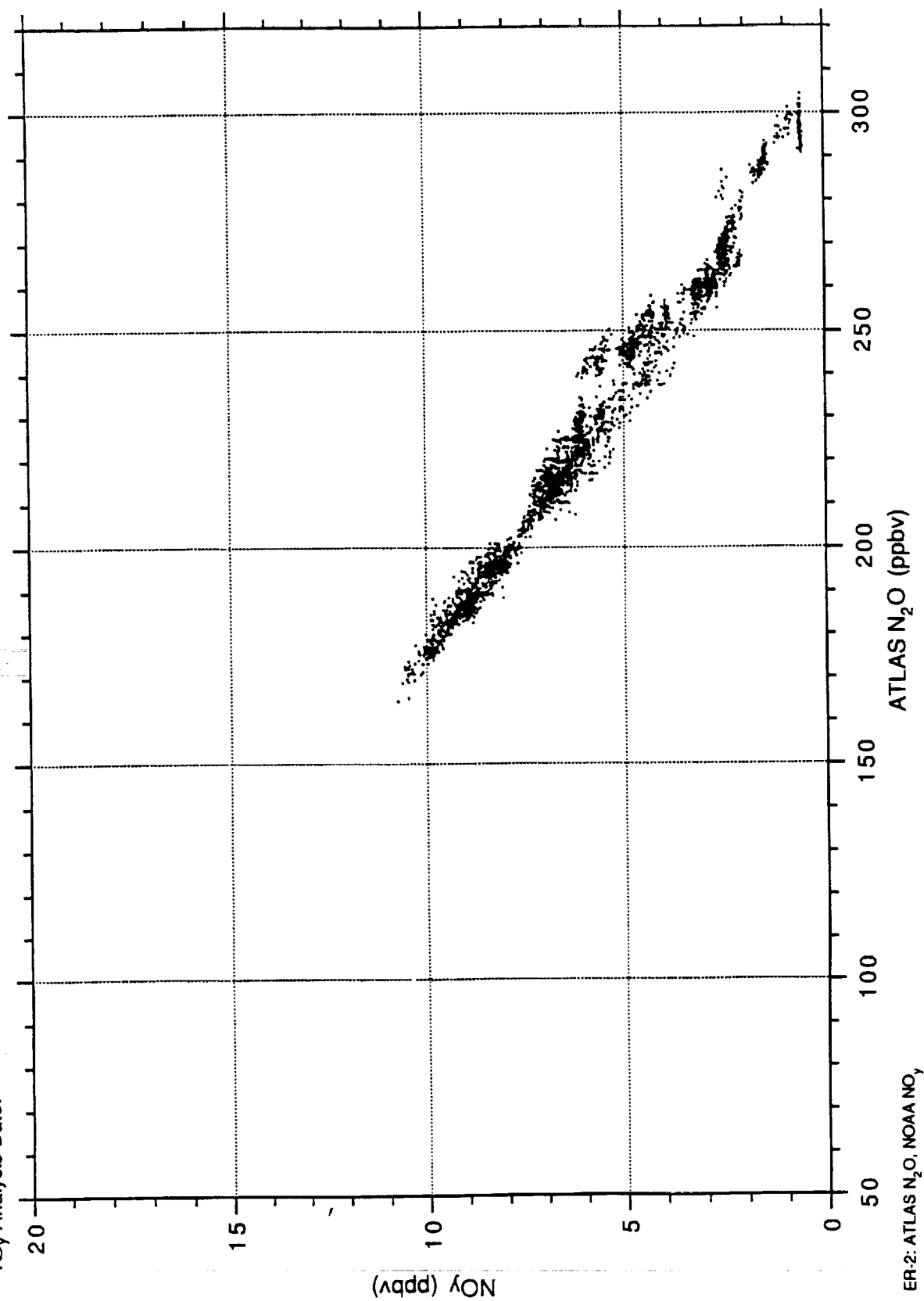
Figure 10.b. NO$_y$ versus N$_2$O for the ER-2 flight of 22 February 1992.
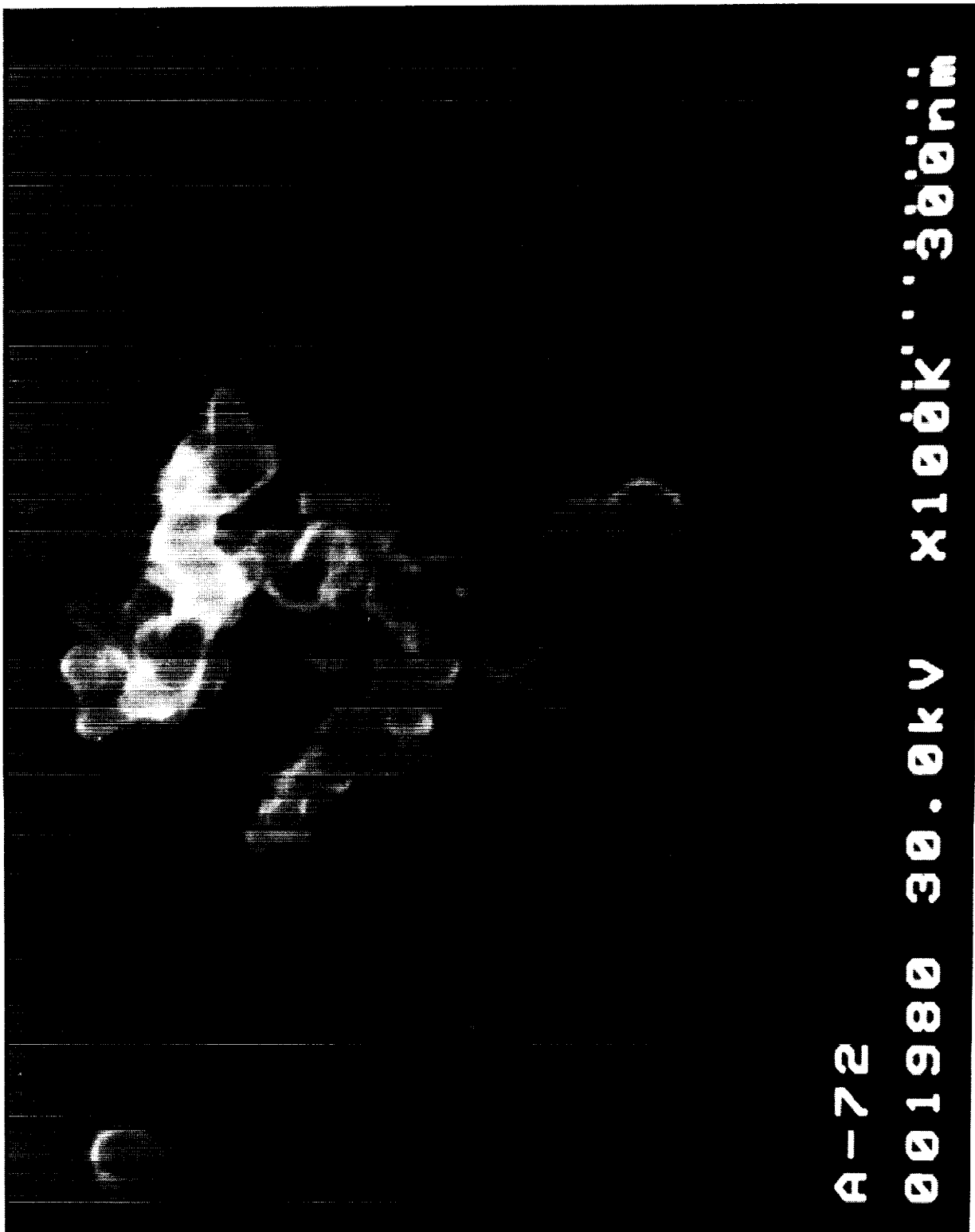
Figure 11a. Black carbon aerosol collected on 23 January 1992 near 68N at 11.3 km MSL altitude.

Figure 11b. Sulfuric acid aerosol collected on 20 March 1992 near 44N at 11.5 km MSL altitude.
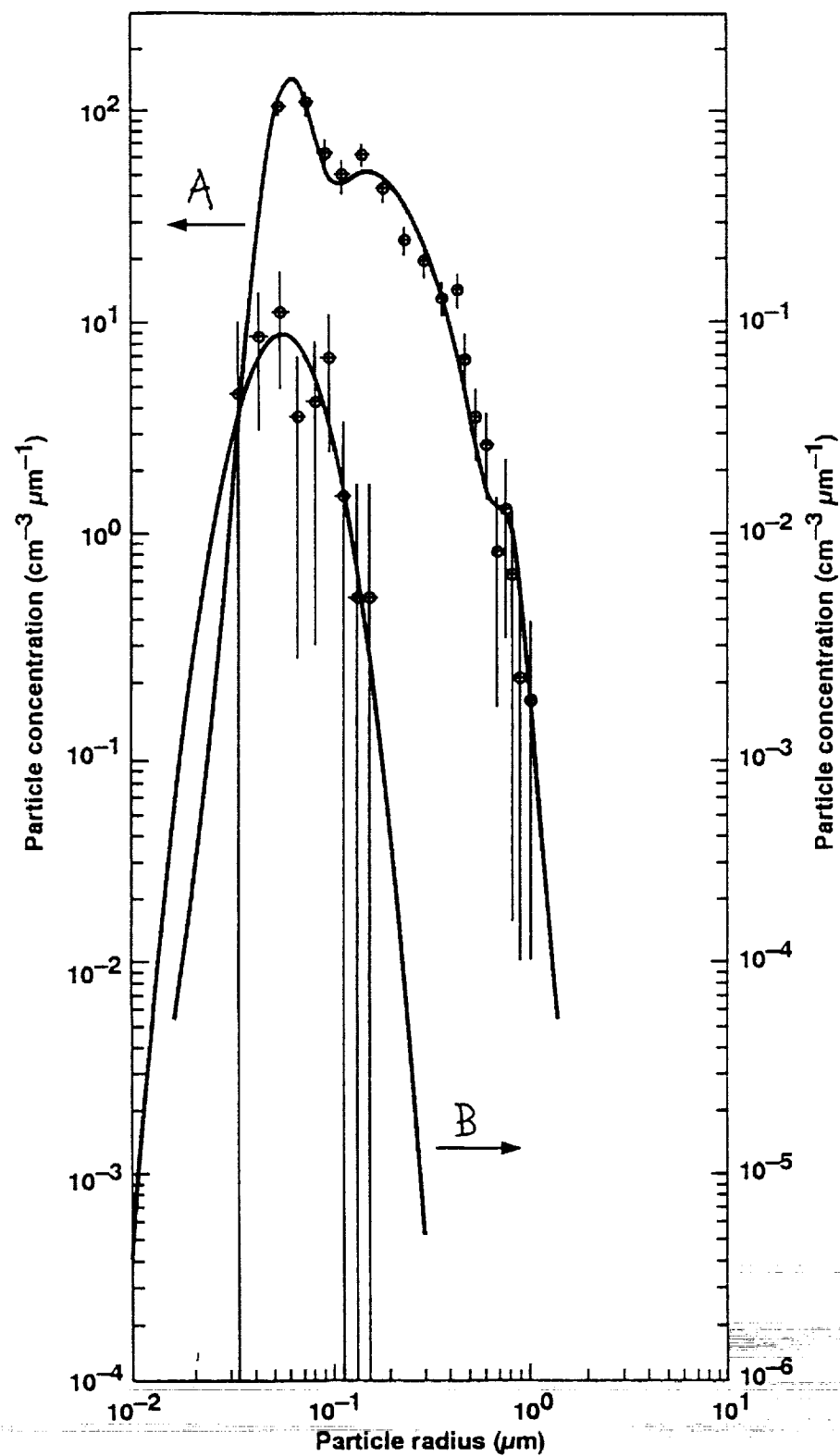
Figure 11c. Aerosol size distribution for black carbon (B) (scale on right) and sulfuric acid (A) (scale on left) aerosols for the flight of 17 February 1992 near 52N at 11.5 km MSL altitude.

Chapter 7

HSRP/AESA Research Summaries

This chapter presents individual summaries of research conducted by investigators supported by High Speed Research Program/Atmospheric Effects of Stratospheric Aircraft as of May 1992; see chapter 1 for an overview of the principal investigators and research areas. The summaries follow this format: (A) title, (B) investigators and institutions, (C) abstract of research objectives, (D) summary of progress and results to date, and (E) journal publications. These summaries have been edited where necessary. The principal investigator (denoted by an asterisk) is the contact person responsible to HSRP/AESA for the proposed research.

HSRP/AESA Principal Investigators

James G. Anderson, Harvard University
Darrel Baumgardner, National Center for Atmospheric Research
Guy P. Brasseur, National Center for Atmospheric Research
William H. Brune, Pennsylvania State University
Karen L. Carleton, Physical Sciences Inc.
David R. Crosley, SRI International
Anne R. Douglass, NASA Goddard Space Flight Center
Timothy J. Dunkerton, Northwest Research Associates
David W. Fahey, NOAA Aeronomy Laboratory
Randall R. Friedl, NASA Jet Propulsion Laboratory
Robert S. Harwood, University of Edinburgh
R. Stephen Hipskind, NASA Ames Research Center
Matthew Hitchman, University of Wisconsin
Ivar S. A. Isaksen, University of Olso
Malcolm K. W. Ko, Atmospheric and Environmental Research, Inc.
Michael N. Kogan, Central Aerohydrodynamics Institute
Charles E. Kolb, Aerodyne Research, Inc.
John S. Langford, Aurora Flight Sciences
Ming-Tuan Leu, NASA Jet Propulsion Laboratory
Max Loewenstein, NASA Ames Research Center
Richard Miake-Lye, Aerodyne Research, Inc.
Mario J. Molina, Massachusetts Institute of Technology
Daniel M. Murphy, NOAA Aeronomy Laboratory
Leonhard Pfister, NASA Ames Research Center
Rudolph F. Pueschel, NASA Ames Research Center
Richard B. Rood, NASA Goddard Space Flight Center

Keith R. Ryan, CSIRO Division of Applied Physics
Robert K. Seals, Jr., NASA Langley Research Center
Patrick J. Sheridan, University of Colorado
Run-Lie Shia, Atmospheric and Environmental Research, Inc.
Margaret A. Tolbert, SRI International
Ka Kit Tung, University of Washington
Richard P. Turco, University of California, Los Angeles
Christopher R. Webster, NASA Jet Propulsion Laboratory
Philip D. Whitefield, University of Missouri-Rolla
James C. Wilson, University of Denver
Stephen C. Wofsy, Harvard University
Douglas R. Worsnop, Aerodyne Research, Inc.
Donald J. Wuebbles, Lawrence Livermore National Laboratory
Glenn K. Yue, NASA Langley Research Center

Development of Solid State Laser System for ER-2 Borne, In Situ Detection of OH and HO$_2$; Supplement to Development of Techniques for the In Situ Observation of OH, HO$_2$, ClO, BrO, ClONO$_2$, O$_3$, P, and T, Between 10 and 30 km for Studies of the Impact of High-Altitude Supersonic Aircraft on the Stratosphere

Investigators

James G. Anderson
Atmospheric Science Project
Engineering Sciences Laboratory
Harvard University
Cambridge, MA 02138

Research Objectives

Our objective is to build an instrument capable of measuring sub-ppt levels of OH and HO$_2$ in the lower stratosphere.

Summary of Progress and Results

A laboratory prototype of the laser system and detection assembly was built and tested. The system was shown to have adequate capability to measure OH in the lower stratosphere. Design of the flight instrument began January 1, and has been nearly completed. Major sub-assemblies are in the process of assembly and test. Test flights are scheduled for 1 October 1992, in order to participate in the SPADE mission scheduled to begin the end of October.

Journal Publications

None

Development of a Prototype Multi-Angle Aerosol Scattering Spectrometer Probe (MASSP)

Investigators

*Darrel Baumgardner
James Dye
Larry Radke
Atmospheric Technology Division
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307-3000

Research Objectives

Our objective is to develop an optical particle counter for the measurement of stratospheric aerosols. The design criteria are as follows: size range from 0.2 to 20 µm, index of refraction discrimination with resolution of 0.02, limited phase (liquid or solid) discrimination, isokinetic sampling, and minimal electronic attenuation at an aircraft velocity of 200 ms^{-1}.

Summary of Progress and Results

The following milestones have been reached:

The theoretical calculations have been completed for determining the optimum collection angles that will provide maximum sensitivity to the aerosol particle index of refraction. The Mie scattering calculations indicate that we should be able to distinguish 2% differences in index of refraction by comparisons of only the forward- and back- scattered components of light scattered from aerosol particles.

The preliminary design of the signal processing electronics has been completed. A design review will be conducted after the photodetectors have been selected for the light collection optics. The new design will process the size and forward-to-back-scatter ratio of each particle and accumulate a matrix of values that will be transmitted periodically to the data system. This matrix of measurements will provide a comprehensive depiction of the aerosol particle size versus index of fraction structure, from which the composition of the particles can be deduced.

The aerosol generation system that will be used for calibrating the MASSP is being constructed at this time. The central element is a taylor cone droplet generator that can produce a monodispersed distribution centered around 1 - 2 µm. This system is presently being characterized for liquids with a variety of indices of refraction.

A preliminary inlet and optical bench configuration have been designed. Wind tunnel studies are in progress for characterizing the flow through models of this inlet system.

Journal Publications

None

Modeling of the Atmospheric Effects of Stratospheric Aircraft

Investigators

*Guy P. Brasseur
Philip J. Rasch
National Center for Atmospheric Research
P. O. Box 3000
1850 Table Mesa Drive
Boulder, CO 80307

Richard P. Turco
Department of Atmospheric Sciences
University of California, Los Angeles
Los Angeles, CA 90024-1565

Research Objectives

In this study we hope to understand and predict the atmospheric effects of a fleet of stratospheric aircraft, using 2-D and 3-D chemical, dynamical, radiative models of the middle atmosphere.

To improve the transport and chemistry formulations in these models and assess the global changes in the atmospheric composition for a variety of scenarios of aircraft emissions.

Summary of Progress and Results

(1) Two-dimensional dynamical and chemical model studies.

The NCAR 2-D model has been further developed to include the effects of heterogeneous chemistry on sulfate aerosol. The impact of high-speed civil transport (HSCT) and CFC injections under these conditions has been studied. We have participated in the recent NASA intercomparison of 2-D models (Models and Measurements Workshop, 2-7 February, 1992, Satellite Beach, Florida). Further improvement are currently being introduced in the model in relation to the transport and radiative schemes.

Model calculations based on NASA scenarios A to G with and without aerosol chemistry have been presented in "Chapter 5, The Atmospheric Effects of Stratospheric Aircraft: A Second Program Report," and at the Meeting on "High Speed Research Program/Atmospheric Effects of Stratospheric Aircraft," 17-22 May 1992, Virginia Beach, VA.

A detailed model study of ozone response to HSCT operations, including the effect of emission altitude and latitude, the chlorine loading, heterogeneous processes, etc., has been completed.

(2) Three-dimensional dynamical and chemical model studies.

A new chemical scheme for the stratosphere has been completed, tested and included in the stratospheric version of the NCAR Community Climate Model. First results obtained by this coupled chemical/radiative/dynamical model have been presented at the "High Speed Research Program/Atmospheric Effects of Stratospheric Aircraft," 17-22 May 1992, Virginia Beach, VA. The 3-D model simulates the behavior of approximately 30 species belonging to the oxygen, hydrogen, nitrogen, and chlorine families. An off-line version of this model is currently being developed and first tests have been completed.

Preliminary simulations of the impact of HSCT have been made with the off-line version of the 3-D model. Zonally symmetric emissions for an inert tracer have been imposed in the lower

stratosphere at different latitudes and the distributions of the tracer have been calculated. Results obtained are significantly different than those obtained from a 2-D model simulation performed for the same missions, especially if the injection takes place near the tropopause. Differences between 3-D runs with zonally averaged and longitudinally dependent emissions have also been investigated.

The offline 3-D transport model has been compared with 3-D online transport to identify the model sensitivity to 1) the sampling strategy in time for winds, and 2) the presence of subgridscale processes like diffusion. The model was also to successfully simulate the transport of Carbon 14 following the scenarios proposed in the above-mentioned Models and Measurements Workshop.

Journal Publications

Brasseur, G. P.: Natural and anthropogenic perturbations of the stratospheric ozone layer, *Planet. Space Sci.*, *40*, 403-412, 1992.

Granier, C. and G. P. Brasseur: Impact of heterogeneous chemistry on model predictions of ozone change, *J. Geophys. Res.*, submitted, 1992.

Brasseur, G. P. and C. Granier: Pinatubo aerosols, chlorofluorocarbons, and ozone depletion, *Science*, in press, 1992.

Tie, X., G. Brasseur, P. Friedlingstein, C. Granier, and P. Rasch, The impact of high altitude aircraft on the ozone layer in the stratosphere, *J. Atmos. Chem.*, submitted, 1992.

Rasch, P. J, X. X. Tie, B. A. Boville, and D. L. Williamson: A three dimensional transport model for the stratosphere, 1992 (to be submitted).

Laboratory Investigations of the Microphysics and Chemistry of Aqueous Particles Typical of the Lower Stratosphere

Investigators

*William H. Brune
Dennis Lamb
Meteorology Department

Bruce R.F. Kendall
Physics Department
Pennsylvania State University
University Park, PA 16802

Research Objectives

The general goal of this project is to investigate the microphysics and chemistry of aqueous particles in a controlled laboratory environment that realistically represent conditions found in the lower stratosphere. More specifically, this task sets out to demonstrate the feasibility of employing the technique of electrodynamic levitation to suspend and isolate micron-sized particles, both liquid and solid, from the influence of chamber walls and yet let the particles be exposed to the air pressure, temperature, moisture, and trace gas environment of the stratosphere. The microphysical investigations focus on the growth rates and phase changes of individual particles as they evolve from small sulfuric acid droplets to hydrated nitric acid crystals under varying humidity and trace gas conditions. Studies of the heterogeneous chemistry will involve swarms of levitated particles to assess the effects of the microphysical properties on the rates and efficiencies of the transformations.

Summary of Progress and Results

Our first efforts in this project, which just got started a few months ago, have been devoted to testing the characteristics of an existing electrodynamic system. Tests for possible electrical breakdown under the reduced pressures needed for experimentation have been successfully completed. Other tests have demonstrated our ability to launch and suspend volatile particles. A new cell has been designed and built to meet our anticipated experimental needs. This cell has interchangeable flat electrodes made of conductive glass, thus simplifying our ability to sense the particle characteristics and position from outside the cell. We are about ready to test the stability of the levitated particles in an externally forced laminar flow of air through the cell and to develop the vacuum and cooling systems.

Journal Publications

None

Heterogeneous Nucleation Kinetics of Atmospheric Aerosols by Single Particle Measurements in a Quadrupole Trap

Investigators

*Karen L. Carleton
David M. Sonnenfroh
W. Terry Rawlins
Physical Sciences Inc.,
20 New England Business Center
Andover, MA 01810

Research Objectives

Heterogeneous atmospheric chemistry is a critical issue in assessing the potential effects of stratospheric aircraft. The demonstrated impact of polar stratospheric clouds on ozone levels suggests that nucleation and growth of aerosols must be considered. This work is designed to measure particle growth rates for single particles under stratospheric conditions in a quadrupole trap. This electrodynamic trap, confines the charged particle in an electric field. The DC voltage across the endcaps of the trap which is necessary to offset the gravitational force on the particle, is proportional to the particle mass. This voltage is measured while exposing the particle to various gas compositions, pressures and temperatures to study particle nucleation and growth kinetics.

Summary of Progress and Results

In the first three months of the program, we have assembled a preliminary version of our quadrupole trap apparatus. The trap is based on a spherical void electrodynamic levitator (SVEL) which is easily machined and has all the same trapping properties as a hyperbolic electrodynamic levitator. The SVEL has several optical ports to introduce a HeNe laser and to collect the scattered light from the suspended particle. The scattered light is imaged with a microscope-based camera system to view the particle.

We have successfully trapped both solid particles, including carbon and polystyrene latex spheres, and liquid particles, including sulfuric acid and sulfate and nitrate salts. We have been working on several methods for optical characterization of the particles, including resolved angular scattering using an optical multichannel analyzer. The angular scattering signatures for these particles can be related to the particle diameter using Mie scattering theory. We have successfully measured scattering patterns for the calibrated polystyrene latex spheres that agree well with their expected particle size.

We are in the process of designing a vacuum version of the trap so that the particle can be exposed to a known gas composition at fixed temperature and pressure. This apparatus will be used for studies of particle nucleation and growth.

Journal Publications

None

Energy Transfer Effects in Laser Detection of Stratospheric Hydroxyl Radicals

Investigators

David R. Crosley
Molecular Physics Laboratory
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025-3493

Research Objectives

Measurement of the hydroxyl radical is essential to testing our understanding of atmospheric photochemistry. In the stratosphere, it can be determined using the method of laser-induced fluorescence, instrumentation for which can be mounted on balloon platforms or the ER-2. Comparing the OH signals measured during a flight with those obtained from a ground-based calibration cell requires knowledge of the fluorescence quantum yield as a function of pressure, temperature, and composition.

A laboratory determination of the needed collisional energy transfer rate coefficients is the objective of this project. Using temporally and spectrally resolved laser-induced fluorescence measurements of OH in cooled flow cells, we will measure the temperature dependence of vibrational energy transfer in the electronically excited state and the final rotational state distribution following vibrational transfer, caused by collisions with nitrogen and oxygen. These data will permit quantitative analysis of OH data over the range of conditions found in the stratosphere.

Summary of Progress and Results

A standard flow cell with provision for inlet cooling has been constructed, although measurements so far have been made only at room temperature. Rate coefficients for total decay from $v=1$ and vibrational transfer from $v=1$ to 0 have been determined for nitrogen and oxygen. For nitrogen, we find agreement with several prior determinations, but our oxygen result is two thirds the presently accepted value.

High-resolution spectral scans provide the final rotational distribution in $v=0$ following the vibrational transfer event. The distributions are nonthermal, with considerable population in high rotational levels. These two apparently kinematically similar colliders behave quite differently: for oxygen, nearly twice as much energy remains in rotation than for nitrogen. This means the effective quenching rate in $v=0$ will be slower than previously assumed, because quenching decreases with increasing rotation. It also explains why the previous result for the oxygen vibrational transfer rate disagrees with ours, because that value was derived assuming a room-temperature distribution in $v=0$.

Distributions for other colliders were measured to understand the vibrational transfer process. Carbon tetrafluoride, nitrous oxide, and carbon dioxide appear similar to nitrogen; hydrogen, deuterium, and methane produce distributions with somewhat less rotation; and argon, surprisingly, behaves very similarly to oxygen.

Journal Publications

None

Two-Dimensional and Three-Dimensional Model Studies of Stratospheric Aircraft Emissions

Investigators

*Anne R. Douglass
Charles H. Jackman
Richard B. Rood
Richard S. Stolarski
Code 916
Atmospheric Chemistry and Dynamics Branch
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, MD 20771

Research Objectives

This research involves the coordinated, parallel use of the NASA/GSFC 2-D model and the 3-D chemistry and transport model (3DCTM). Chemical assessments of the impact of aircraft exhaust on stratospheric ozone employ the 2-D model. In addition to examining required scenarios, the 2-D model is being used for photochemical and transport sensitivity studies. Chemical issues under consideration include the impact of heterogeneous processes, the comparison of calculated values with measurements, and the possibility that increased odd nitrogen and water vapor in flight corridors may lead to an increased probability of nitric acid trihydrate clouds outside the polar vortex. Because the size of the perturbation for any exhaust product depends upon its residence time in the lower stratosphere, the model sensitivity to lower stratospheric transport is of particular importance. The 3-D dispersion of tracers is being examined using the 3DCTM. This model uses winds from a data assimilation procedure and provides a realistic simulation of tracer dispersion. The modeled behavior of tracers and species such as ozone is being compared with satellite fields as a means of model validation. Long (greater than 1 year) calculations for inert tracers allow us to determine the altitude, latitude, and seasonal dependence of horizontal and vertical tracer transport, and to provide estimates of the potential buildup of pollutants in oceanic flight corridors. Such calculations also allow a direct comparison of 2-D and seasonally averaged 3-D transports. These calculations should serve to reduce the uncertainty in assessments associated with 2-D model transport.

Summary of Progress and Results

All scenarios requested by the program have been completed using the 2-D model. For gas phase calculations, the sensitivity of model results to the transport has been evaluated (Jackman et al., 1991). Comparisons of calculated values with carbon-14 and Total Ozone Mapping Spectrometer (TOMS) measurements indicated the importance of using a representation of diffusive transport that is consistent with the other dynamical fields in the 2-D model; we have implemented such a scheme in our model. Heterogeneous chemical reactions have also been included in the model; these have the effect of reducing the impact of NO_x emissions by speeding up the conversion of NO_x to the reservoir species HNO_3. We participated in the Models and Measurements Workshop held in February, 1992 at Satellite Beach, FL. These comparisons suggest the importance of improving 2-D models so that the high-latitude processes may be more faithfully represented.

The 3-D model has been used to examine the evolution of tracer fields for a zonally symmetric source; this situation is most directly comparable to a 2-D model. A more realistic situation has also been examined, in which aircraft are confined to northern Atlantic, northern Pacific, and tropical oceanic corridors. The 3-D model indicates the importance of middle latitude synoptic-scale events to stratosphere/troposphere exchange. Exchange is found to be comparable for the

three corridors, in contrast to 2-D calculations which suggest much more rapid transport to the troposphere for high latitude sources.

Journal Publications

Jackman, Charles H., Anne R. Douglass, Kurt F. Brueske, and Stephen A. Klein, The influence of dynamics on two-dimensional model results: Simulations of 14C and stratospheric aircraft NO_x injections, *J. Geophys. Res.*, *96*, 22559-22572, 1991.

Douglass, Anne R. and Richard B. Rood, The dynamics of the HSCT Environment, Proceedings of AIAA Aircraft and Design Systems Meeting, Baltimore, MD, 1991.

Rood, Richard B., Anne R. Douglass, and Clark J. Weaver, Tracer exchange between tropics and middle latitudes, *Geophys. Res. Lett.*, *19*, 805-808, 1992.

Weaver, Clark J., Anne R. Douglass, and Richard B. Rood, Thermodynamic balance of three-dimensional stratospheric winds derived from a data assimilation procedure, submitted to *J. Atmos. Sci.*, 1992.

Douglass, Anne R., Richard B. Rood, Clark J. Weaver, Mark Cerniglia, and Kurt F. Brueske, Implications of 3-D tracer studies for 2-D assessments of the impact of supersonic aircraft on stratospheric ozone, to be submitted to *J. Geophys. Res.*, 1992.

165

Inertia-Gravity Waves in the Stratosphere: Excitation, Propagation, and Constituent Transport

Investigators

*Timothy J. Dunkerton
Donal O'Sullivan
Northwest Research Associates
P. O. Box 3027
Bellevue, WA 98009

Research Objectives

This study seeks to understand better the excitation of internal inertia-gravity waves in the troposphere, their subsequent propagation and breakdown in the lower stratosphere, generation of secondary instabilities, and resulting vertical transport of trace constituents. Such transport is essential for the removal of exhaust pollutants produced by future high-speed aircraft in order to lessen the severity of ozone depletion. We focus specifically on the role of middle latitude synoptic-scale weather systems (baroclinic instability and frontogenesis) in excitation of IGW, refraction into regions of preferred wavebreaking, and the efficiency of in situ mixing by convective and dynamical instabilities in breaking IGW.

Summary of Progress and Results

Because we have recently begun our research project in this area, we are still in the initial stages of the proposed work. We have begun to perform baroclinic life-cycle experiments with a global version of the NASA Ames 3-D model. We have also modified the model into a sector model (60 degree longitudinal span) in preparation for higher resolution life-cycle experiments. During the coming months we plan to continue the high-resolution experiments, testing various vertical resolutions in order to refine the problem sufficiently to the point where we will be able to explicitly resolve inertia-gravity wave excitation and propagation due to cyclogenesis and frontogenesis.

Journal Publications

None

ER-2 Lower Stratospheric Studies of Chemistry and Dynamics

Investigators

*D. W. Fahey
K. K. Kelly
M. H. Proffitt
A. F. Tuck
R/E/AL6
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303-3328

Research Objectives

The problem is to understand how the lower stratosphere will respond to chemical inputs from the jet engines of supersonic transport aircraft. This will be accomplished by first understanding how the ambient lower stratosphere maintains its composition. Although great progress resulted from AAOE and AASE, there are still many outstanding problems. The immediate objectives are to analyze the recent data from AASE-II, participate in the upcoming SPADE and ASHOM campaign and obtain understanding from them by studying the results, with particular reference to NO, NO_y, H_2O, and O_3.

Summary of Progress and Results

The dominant activity within the period of the funding (i.e., since 911231) has been the latter stages of AASE-II and the initial data analysis. Efforts are being made to recruit postdoctoral workers who will be involved in SPADE and ASHOM during 1992-1994. The ozone instrument has been repackaged to achieve an approximately 50% weight reduction and will participate in the upcoming test flights for the new and modified instruments in the SPADE payload in August at NASA Ames (Proffitt).

Journal Publications

There have been no publications yet that result from HSRP funding.

Chemical Kinetics Studies of Hydrocarbons from Stratospheric Aircraft

Investigators

*Randall R. Friedl
Stanley P. Sander
William B. DeMore
Mail Stop 183-901
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109

Research Objectives

We are collecting experimental data on the rates and mechanisms of key elementary gas-phase and gas-surface reactions that relate to the processing of nonmethane hydrocarbon aircraft exhaust in the lower stratosphere. Our focus is on processes that may impact the partitioning of nitrogen oxides. Consequently, we have been investigating chemical production and loss mechanisms of peroxyacetyl nitrate (PAN), an important reservoir of odd nitrogen in the atmosphere and a common intermediate in the atmospheric oxidation of small nonmethane hydrocarbons.

Summary of Progress and Results

Experimental results were obtained for two potentially important stratospheric loss processes of PAN, namely, reaction on solid H_2O-ice surfaces and photolysis.

Characterization of the heterogeneous reaction properties of PAN was facilitated by the development of a novel gas-flow switching technique. This technique allowed us to rapidly switch the PAN flow from downstream to upstream of the ice surface, and vice versa. Using this method, transient adsorption processes on subsecond timescales were characterized and subsequently differentiated from irreversible reactive processes. Application of this technique to PAN revealed that the uptake coefficient is approximately 10^{-3} on fresh H_2O-ice surface. Saturation of the surface is rapid, however, and the process is reversible. The amount of PAN adsorbed is proportional to the gas phase concentration of PAN; it is roughly 0.01 mg per g of H_2O for a PAN concentration on the order of 10^{12} cm^{-3}. There is no evidence for chemical reaction of PAN on the ice. We estimate an upper limit of 10^{-5} for the sticking coefficient associated with irreversible chemical reaction.

The role of physically adsorbed PAN on stratospheric aerosols deserves further scrutiny. We estimate that under lower stratospheric conditions ice particles should consist of approximately 10^{-5} monolayers of PAN or 0.1% of the gas phase concentration.

During the last year construction of a laboratory apparatus designed for studies of PAN photolysis was completed. Measurements of the NO_2 product yield from PAN photolysis at 248 nm are currently underway. A preliminary value of 0.8 ± 0.2 has been obtained. The atmospheric implication of this finding is that PAN is essentially a reversible reservoir of NO_2 with respect to photolysis.

Journal Publications

None

The Environmental Impact of High-Flying Aircraft Studies Using Two-Dimensional Models

Investigators

*Robert S. Harwood
Jonathan S. Kinnersley
Department of Meteorology
James Clerk Maxwell Building
University of Edinburgh
Mayfield Road
Edinburgh, EH9 3JZ
UK

John A. Pyle
Anna E. Jones
Department of Chemistry
University of Cambridge
Lensfield Road
Cambridge, CB2 1EW
UK

Research Objectives

The effects of a proposed supersonic, civil aircraft on the stratosphere will be assessed using 2-D models containing as many as possible of the important interactions between chemistry and dynamics. The Edinburgh group is concentrating on developing the dynamical formulation of a highly interactive version of the model, exploiting the practical benefits of isentropic coordinates to parametrize the large effects of planetary waves. The Cambridge group is concentrating on enhancing the homogeneous and heterogeneous chemistry and a treatment of aerosol processes, initially using a Eulerian formulation of the model. At appropriate stages the new chemistry and dynamics are merged into a single model for the assessment studies.

Summary of Progress and Results

At the time of the first annual report, the new dynamical formulation was running with PV fluxes specified from climatology. Since that report an interactive parametrization of these fluxes has been introduced in which the distributions of the three gravest planetary waves are calculated in the stratosphere consistent with prescribed values at the tropopause and the mean stratospheric state, these distributions being used to infer transports of PV and species. This model, together with the chemical scheme available at the time, was used in the Model Intercomparison Workshop.

During the last year, the Cambridge group has investigated the effect on the destruction of O_3 by NO_x of the presence of aerosol and of new temperature-dependent photolysis rates for HNO_3. The new data lead to significant reduction of the O_3 destruction and, in certain locations, O_3 production of ozone by NO_x is calculated.

Journal Publications

Bekki S., Toumi R., Pyle, J. A. and Jones, A. E., Future aircraft and global ozone, *Nature, 345*, 193-194., 1991

Bekki, S. and Pyle, J. A., 2-D assessment of the impact of aircraft sulphur emissions on the stratospheric sulphate aerosol layer, *J. Geophys. Res.* (to appear).

Kinnersley, J. and Harwood, R. S., A 2-D isentropic model with an interactive planetary wave parametrization, submitted to *Q. J. Roy. Met. Soc.*

Data Management and Meteorological Support for HSRP Aircraft Field Campaigns

Investigators

*R. Stephen Hipskind
Patricia Hathaway
Steven E. Gaines
Mail Stop 245-5
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035-1000

Research Objectives

The objective of this study is to provide mission support, including both data management and meteorological support for aircraft field campaigns. Data management entails providing format standards for data exchange, obtaining and archiving field data, and reproducing the data for distribution. Meteorological support entails obtaining conventional analysis and forecast data for mission planning, as well as obtaining real-time meteorological satellite imagery using the Ames Meteorological Satellite Downlink and Display System (MSDDS).

Summary of Progress and Results

The data exchange for the second Airborne Arctic Stratospheric Expedition (AASE II) was accomplished for the first time via a local area ethernet network using automated submission and format checking routines. The data exchange process worked very well and will be implemented for the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE). The mission dataset for AASE II has been published on CDROM, as will the dataset for SPADE.

The meteorological support for AASE II, SPADE and future HSRP/AESA field missions consists of providing real-time meteorological satellite imagery via MSDDS. This system was deployed for the first time for AASE II and worked extremely well, providing both a surface weather forecast tool as well as digital radiance and albedo measurements for scientific analysis. In addition to MSDDS a satellite receiver was deployed for AASE II to acquire and print weather charts from the National Meteorological Center.

Journal Publications

AASE II Mission Dataset CDROM, July 1992, S. Gaines, P. Hathaway, S. Hipskind, Eds., UARP-004.

Dynamical and Chemical Studies of Aircraft Emissions Using Satellite Data and a 2-D Model

Investigators

Matthew Hitchman
Department of Meteorology
1225 West Dayton Street
University of Wisconsin, Madison
Madison, WI 53706

Research Objectives

We are employing satellite and aircraft data and a fully interactive 2-D model of the middle atmosphere to study the heterogeneous effects of sulfate aerosols and wave effects on tracer transport. Climatological distributions of SAGE and SAM II aerosol will be calculated and used with recent reaction-rate estimates in the model to assess potential ozone loss for various scenarios. The circulation of lower stratosphere - upper troposphere will be reassessed in the model, with particular attention paid to vertical mixing by inertio-gravity waves, Rossby waves, and the zonal mean meridonal circulation.

Summary of Progress and Results

Our grant began on 1 March 1992 and supports Ms. Megan McKay, a graduate research assistant. Employing SAGE and SAM II satellite date for the period 1979-1991, we have calculated climatological distributions of aerosol extinction, extinction ratio, and surface density by month and by the phase of the quasibiennial oscillation (QBO). The treatment of Rossby waves was extended to include mechanical dissipation during the wave breaking process. Sudden warmings may be obtained by changing the wave forcing, degree of poleward refraction or magnitude of dissipation, and such events alter constituent transport. Model runs were performed to assess the various effects of surface anthropogenic trace gases, aircraft emissions, and unusual volcanic events, with and without heterogeneous chemistry, the seasonal aerosol cycle, the QBO aerosol cycle, and variations in Rossby wave transport. Results were reported at the HSRP meeting in Virginia Beach.

Journal Publications

Hitchman, M. H., M. A. McKay, and C. R. Trepte, 1992 "Circulation deduced from aerosol data averaged by season and phase of the quasibiennial oscillation," in *Coupling Processes in the Lower and Middle Atmosphere*, Kluver Academic Publishers, in press.

The Impact of NO_x Emission on Ozone from a Future Fleet of High Flying Aircraft

Investigators

Ivar S. A. Isaksen
Institute of Geophysics
University of Oslo
P. O. Box 1022 Blindern
0315 Oslo 3
NORWAY

Research Objectives

The objectives have been to study the impact on ozone of NO_x emitted from a future fleet of supersonic aircraft flying in the lower stratosphere, and to study the sensitivity of the ozone perturbations to heterogeneous chemistry in the lower stratosphere and to the stratospheric chlorine loading. Heterogeneous chemistry primarily affects speciation of chlorine compounds and chlorine loading through the strong linkage of the NO_x chemistry in the lower stratosphere with the chlorine chemistry through the reaction of ClO with NO_2. Therefore, a main task is to study how the heterogeneously induced ozone reduction by chlorine and bromine reactions in the lower stratosphere is affected by enhanced NO_x emission.

Summary of Progress and Results

The parameterization of the heterogeneous chemistry in the model is updated to include the recently updated values for reactions of nitrogen and chlorine compounds on particles in the stratosphere. Heterogeneous reactions of N_2O_5, $ClONO_2$, HCl, and $HOCl$ on background particles and on PSCs are included in the calculations. Time-dependent calculations until 2025 are performed for a base case where NO_x emissions from supersonic aircraft are not included. Several model calculations with NO_x emission from supersonic aircraft are also done. In these calculations the height of the emission is varied corresponding to a speed of 1.6 to 2.4 Mach, and two different emission indices (5 to 15 g $[NO_2]$/kg fuel) are used. The results of the NO_x perturbations are also compared with the CFC and halon impact on ozone in 2025.

The 2-D model calculations with the adopted scenarios resulted in small changes in ozone column densities from stratospheric NO_x emissions, even at high northern latitudes where the largest impact is calculated to occur. The reduction in ozone column densities is always less than 1%. We find that the efficient loss of ozone through chlorine and bromine reactions in the lower stratosphere that is initiated by heterogeneous chlorine and nitrogen chemistry is markedly reduced when additional nitrogen is emitted from aircraft. This is due to the nitrogen-chlorine interaction which reduces the abundancies of ClO. This decreased loss compensates for the NO_x-induced loss at higher altitudes. The sensitivity of NO_x perturbation to the heterogeneous processes and to the chlorine loading of the stratosphere is being investigated at present.

Journal Publications

Results of the study are being prepared for publication.

Three-Dimensional Transport of Emission Products from High-Speed Stratospheric Aircraft by Large-Scale Winds: Construction of Appropriate Source Functions for 2-D Assessment Models

Investigators

*Malcolm K. W. Ko
*Run-Lie Shia
Rao Kotamarthi
Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, MA 02139

Research Objectives

Emissions from high-speed stratospheric aircraft are localized sources of tracer material for the stratosphere. Within 10 to 20 days after emission, the material is redistributed zonally, as well as latitudinally, by the large-scale wind field. If 2-D models are used for the assessment of the long-term impact of high-altitude flights, it is necessary to have zonal-mean source functions that take into account the initial redistribution. We study the large-scale redistribution using two methods. In the first approach, we simulate the transport of the deposited material on isentropic surfaces, assuming that the material stays on the isentropic surface on which it was deposited for time periods of the order of 20 days. In the second approach, we obtain the zonal-mean distribution of the deposited material by examining the average coordinates of the deposited material in the potential-temperature and potential vorticity space. The 8 years of National Meteorological Center daily temperature and geopotential height analyses, extending from 1000 to 0.4 mb, are used in both methods. By calculating the initial transient adjustment of the tracer field for a large number of episodes and different flight paths, appropriate average source functions for 2-D models for different times of the year will be constructed. Sensitivity studies will be performed to examine the role of small-scale diffusion, the effects of motion through the isentropes, and the resolution needed to adequately describe tracer transport in the lower stratosphere.

Summary of Progress and Results

To simulate the transport on isentropic surfaces, we initially adapted the 3-D transport model of Schneider (*Mon. Wea. Rev.*, 112, 1206, 1984), which utilizes the square root scheme. It has been modified to use the Prather scheme (Prather, *JGR*, 91, 6671, 1986), which produces much less numerical diffusion for tracer distributions with large spacial gradients. Experiments were performed in a 5°(longitude)x2°(latitude) grid using winds from two seasons to simulate the redistribution of an idealized source function (zonally symmetric) and source functions representing actual flight paths. Our results indicate that the latitudinal transport by large-scale winds is important not only in the winter, but in the summer cases as well. If zonal averages of the tracer mixing ratio are calculated, the latitudinal gradient north of 40 N vanishes after about 10 days in the winter and after 20 days in the summer cases considered. In all cases, the tracer distribution becomes zonally homogeneous, to a great extent after 10 to 15 days. Variations along longitude circles are typically of the order of 30%.

The experiments were repeated using (1°x1°) resolution and there are no noticeable differences compared with results calculated with (5° x 2°) resolution for the idealized source. We plan to repeat the flight path calculation in (1°x1°) model to investigate the effects of small-scale transport.

In collaboration with Professor R. A. Plumb from MIT, we developed an alternative method to simulate the initial redistribution. The NMC data are used to calculate the potential temperature

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(Θ) and potential vorticity (PV) along the flight path as a function of time. The emitted material is sorted according to Θ and PV along the flight path. After the material has accumulated in Θ-PV space for a certain period of time (now taken to be 20 days), the distribution in the Θ-PV space is used to calculate the averaged latitude and altitude of the emitted material. Work is in progress to compare the results from the two approaches.

There are limitations to these approaches, one of them being that they do not work too well for flight paths that cross the tropics. We will be looking for alternate methods for those regions.

Journal Publications

Plumb, R. A. and M. K. W. Ko, (1992) Interrelationships between mixing ratios of long lived stratospheric constituents. J. *Geophys. Res.*, 97, 10,145-10,156.

Investigation of Nonequilibrium Physical and Chemical Processes in the Stratospheric and SST Wake: Investigation of Heterogeneous Processes in Porous Aerosols

Investigators

*Michael N. Kogan
Alexander P. Kuriachy
Yuri E. Markachev
Albert L. Stasenko
Eugeny A. Surdutovich
Central Aerohydrodynamics Institute (TsAGI)
Zhukovsky, Moscow Region
140160
RUSSIA

Research Objectives

The primary purpose is to estimate theoretically different characteristic time-scales of the homogeneous and heterogeneous physical and chemical processes that take place in the jets and wakes of stratospheric aircraft. Then, on this basis, to develop a flight test program for verification of these theoretical models and assessment of high-altitude aviation impact on the ozone layer.

Summary of Progress and Results

Concentration of ecologically harmful exhausts from scramjet engine has been determined, taking into account irreversible processes in combustion chamber and nozzle.

A mathematical model has been proposed to describe the absorption of nitrogen oxide by water drops condensed in an axisymmetric jet of a flying vehicle. Surface adsorption characteristics of porous particles was determined.

A simple kinematics model of the impact of 3-D trailing vortices on the jets of aircraft has been proposed, which will facilitate the further wake investigations on the basis of Navier-Stokes equations.

The up-to-date chemical-radiative-transport models of stratosphere and mesosphere have been reviewed and non-equilibrium parameters of vibrationally and electronically excited gas species have been calculated.

Journals and Publications

Kogan, M. N. and Z. M. Malikov, Influence of Aircraft Flight on Harmful Pollution Transfer in the Stratosphere, reprints of TsAGI no. 33, 1991.

Stasenko, A. L., Contribution to the Theory of Chemisorption of Nitrogen Oxides by Water Drops in a Jet of Stratospheric Aircraft, reprints of TsAGI no. 51, 1991.

Stasenko, A. L., An Aircraft in the Ozone Layer, Kvant, Popular Magazine on Phys. and Math., ed. Nauka Acad. Sci., NN 5 and 6, 1992.

Stasenko, A. L., High-Altitude Civil Aviation Impact on the Ozone Layer: Theory and Flight Experiments Planned, Second Annual Meeting on HSRP/AESA, Virginia Beach, VA, May 17-22, 1992, Abstracts.

Egorov, B. V., Yu. E. Markachev, Nonequilibrium Photochemistry of Stratosphere and Mesosphere, ibidem.

Egorov, B. V., V. N. Komarov, Yu. E. Markachev, Scramjet and Ecologic Problems of Stratosphere, preprints of TsAGI no. 57, 1992.

Grinats, E. S., A. L. Stasenko, Simulation of Trailing Vortices Impact on the Aircraft Jets and Chemisorption of Nitrogen Oxides by Water Droplets, preprints of TsAGI, 1992, in press.

Plume Chemistry and Dispersion Modeling to Evaluate the Atmospheric Effects of Stratospheric Aircraft

Investigators

*C. E. Kolb
R. C. Brown,
R. C. Miake-Lye
M. Martinez-Sanchez†
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821-3976

†M. Martinez-Sanchez is also associated with the
Department of Aeronautics and Astronautics
Massachusetts Institute of Technology
Cambridge, MA 02139

Research Objectives

The exhaust gases from prospective, advance high-altitude supersonic aircraft will be rich in nitrogen oxides (NO_x), water vapor, sulfur oxides (SO_x), carbon monoxide, condensation nuclei, and other trace species when compared with ambient stratospheric air. As these exhaust gases mix with the ambient air, a complex series of fluid dynamic and radiative processes will spread the exhaust trail both laterally and vertically and may raise or lower the exhaust plume/ambient mixture in altitude. Exhaust plume chemistry will tend to oxidize NO_x to NO_3, HNO_3, and perhaps N_2O_5, and SO_x to SO_3 and perhaps H_2SO_4; these oxidative species may, in turn, activate exhaust soot particles to cloud (contrail) condensation nuclei. Wingtip vortices will entrain and confine the exhaust plumes, cooling them by centripetally driven pressure drops. The exhaust water vapor may condense into ice contrails providing active surfaces for environmentally important trace species, including HNO_3, $ClNO_3$, N_2O_5, HCl, H_2SO_4, etc., changing the chemical speciation in the exhaust-perturbed air. Furthermore, contrail particles may grow to sufficient size to settle gravitationally, displacing water and possibly other trace species, such as HNO_3, to lower altitudes. Since the chemistry and dynamics of the exhaust plume may significantly impact the inputs to large-scale 2-D and 3-D assessment models, it is necessary to assess systematically the chemical and physical processes driving the plume and its dispersion. The goal of this project is to model the major physical and chemical processes occurring in the aircraft exhaust plumes, wake vortices, and entrained ambient atmosphere to connect intelligently what will issue from aircraft engine nozzles to large-scale photochemical models of the stratosphere.

Summary of Progress and Results

The chemical, radiative, and fluid dynamic processes important to this project divide naturally into three regimes: the exhaust plume region, the vortex wake regime, and the wake dispersal process. During the second year, we have continued modeling and/or analysis activities in all three areas. The highlights are summarized below.

Exhaust Plumes: Homogeneous chemical and equilibrium condensation calculations were refined, building on previous results. In order to model the growth of contrail particles to characterize their ability to sediment and the surface area they offer for heterogeneous chemistry, a condensation kinetics model has been incorporated into the Standard Plume Flowfield (SPF) reacting flow plume numerical model. This condensation kinetics scheme is based on the model of Hoshizaki, et al. (H. Hoshizaki, et al., 1978; J. W. Meyer, 1979). Calculations using this condensation kinetics model in SPF were performed where the condensation nuclei

concentrations were varied parametrically to explore the effects of degree of activation of soot particles as well as their total number density. Particle growth and reevaporation were followed as was total amount of condensed water. Particle sizes remained too small for sedimentation, but particle number density and total condensed water depend almost linearly on the number density of active condensation nuclei.

Wake Vortices: Calculations of the entrainment, confinement, and local cooling in the trailing vortices were refined to be more representative of projected HSCT configurations. Capture of the exhaust plumes depends on engine placement, with locations closer to the wingtip being entrained faster than those closer to the fuselage. Both locations considered are captured before instabilities in the trailing vortex system cause it to breakup and reconnect as distorted vortex rings. Subsequent evolution of the distorted vortex rings after contrail break up is approximated based on measurements of turbulent vortex rings (A. Glezer and D. Coles, 1990) which indicate a significant lifetime of organized motion after the trailing vortex system reconnects. This phase of the wake continues to confine and transport the exhaust. Estimates of the cooling near the core of the trailing vortices indicate that the maximum atmospheric temperature for which contrails are expected to form is increased by about 2 K relative to models that do not include dynamical effects in the vortex cores.

Wake Dispersal Regime: The Lagrangian box model calculations of the wake dispersal have been extended to a time period of two days to investigate the sensitivity of the results to different assumptions about scale-dependent dispersion. The calculations indicate that a chemically perturbed environment could persist for two days after the passage of the aircraft. In particular, concentrations of radiatively important species such as ozone and water could be reduced by about 20% and enhanced by factors of 4-70, respectively, during this period. Calculations of the radiative balance in this perturbed air mass indicate that differential cooling rates relative to background could approach 10 K/day, leading to downward velocities of up to 0.2 to 1 km/day. These estimates depend critically on the adopted rates of dispersion, and information about this parameter is almost non-existent. Other processes not included in the present formulation, such as random shear, may be equally important and could lead to faster dispersion. Estimates for time constants due to random strain are also unknown, with estimates spanning 1-10 days.

Journal Publications

Miake-Lye, R. C., R. C. Brown, M. Martinez-Sanchez, and C. E. Kolb, Plume and wake dynamics, mixing and chemistry behind an HSCT aircraft, *J. Aircraft*, in press.

Rodriguez, J. M., R. L. Shia, M. K. W. Ko, C. W. Heisey, R. C. Miake-Lye, and C. E. Kolb, Photochemistry and Radiative Cooling of Wakes from High-Altitude Aircraft, manuscript in preparation.

Brown, R. C., R. C. Miake-Lye, and C. E. Kolb, Heterogeneous Condensation in Stratospheric Aircraft Plumes: Model Simulations for an HSCT Aircraft, manuscript in preparation.

In Situ Measurement Platform for Altitudes Exceeding 25 km

Investigators

John S. Langford
Aurora Flight Sciences
10601 Observation Road
Manassas, VA 22111

Research Objectives

Validating global chemical models and 3-D chemical transport models requires in situ measurements of tracers and free radicals at a variety of locations and at altitudes up to 30 km. Aurora is developing the Perseus A remotely piloted aircraft to carry small payloads to very high altitudes in time for use in the 1994 measurement campaigns.

Summary of Progress and Results

Recent milestones in the Perseus project include:

- Funding started on 17 September 1991.

- A full-scale proof-of-concept aircraft was successfully flown at El Mirage, California in November 1991.

- A Preliminary Design review was held at Aurora on 4 February, 1992.

- The full-scale closed-cycle propulsion system ran for the first time on 11 May 1992.

- The Critical Design review was successfully completed on 29 May 1992.

- Wing article #1 was completed and proof tested on 21 July 1992.

Aurora is presently planning to conduct initial test flights on the high-altitude Perseus A during the first quarter of 1993.

Journal Publications

Small High-Altitude Science Aircraft Technical Design and Development Report, 28 May 1992.

Preston C. S., S. P. Hendrickson, and J. S. Langford, A Closed Cycle, High-Altitude Rotary Engine for Unmanned Ozone Sampler, SAE Technical Paper #921548, August 1992.

Russell P., J. Langford, J. Anderson, D. Lux, D. W. Hall, and S. Wegener, Advanced Aircraft for Atmospheric Research, AIAA Paper # 91-3162, September 1991.

PERSEUS PAYLOAD USER'S GUIDE, Version 2.0, May 1992.

Laboratory Studies of Heterogeneous Processes Important in Stratospheric Aircraft Emissions

Investigators

*Ming-Tuan Leu
Leon F. Keyser
Liang Chu
Jet Propulsion Laboratory
National Aeronautics and Space Administration
4800 Oak Grove Drive
Pasadena, CA 91109

Research Objectives

This task focuses on heterogeneous processes that are potentially important in assessing the environmental impacts of high-altitude aircraft emissions. The work aims to investigate the effects of water ice, nitric acid trihydrate, sulfuric acid aerosol, and soot on atmospheric species important in the ClO_x, NO_x, and HO_x cycles that include: HCl, ClO, $ClONO_2$, NO, NO_2, O_3, N_2O_5, HNO_3, OH, HO_2, H_2O_2, and SO_2. Low actor mass spectrometry and discharge flow resonance fluorescence are used to measure sticking or reaction probabilities on these aerosols. Several analytical techniques, which include mass spectrometry, chloride ion electrode, infrared absorption, scanning electron microscopy, X-ray diffraction spectrometry, and BET surface area analysis, are employed to identify products and characterize the condensed phase.

Summary of Progress and Results

The uptake of HCl in water ice and nitric acid trihydrate (NAT) films has been investigated in a flow reactor interfaced with a differentially pumped quadrupole mass spectrometer. These studies are performed under experimental conditions that mimic the polar stratosphere. The mole fraction of HCl absorbed in ice crystals at 188 K and 193 K is determined to be in the range of 7×10^{-6} to 2×10^{-4} when HCl partial pressures of 6×10^{-8} to 5×10^{-6} torr are used. The uptake of HCl in NAT at 188 K is also measured to be in the range of 5×10^{-6} to 1×10^{-4} in units of mole fraction at the HCl partial pressures from 1×10^{-7} to 2×10^{-6} torr.

Journal Publications

Leu, M-T., S. B. Moore, and L. F. Keyser, Heterogeneous reactions of hydrogen chloride on type I polar stratospheric clouds, *J. Phys. Chem., 95,* 7763, 1991.

Keyser, L. F. and M-T. Leu, Surface areas and porosities of ices used to simulate stratospheric clouds, *J. Coll. Interface Sci.,* in press, 1992.

Chu, L. T. and M-T. Leu, Uptake of HCl in water ice and nitric acid trihydrate films, submitted to *J. Phys. Chem.,* 1992.

ARGUS: A Dual Channel Tracer Instrument for Stratospheric N_2O and CH_4 Measurements

Investigators

Max Loewenstein
Mail Stop 245-5
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035-1000

Summary of Progress and Results

The dual channel tracer instrument, dubbed Argus, was funded in the first quarter of FY 1992. The instrument is being designed to provide tracer measurement capability on the Perseus aircraft platform primarily for stratospheric research in the framework of the AESA element of the HSRP. This new tracer instrument will be capable of providing high accuracy (~3%) atmospheric measurements of N_2O and CH_4 from the surface to 25 km altitude at any latitude from which Perseus will in the future be deployed. To provide the greatest flexibility of application of this new instrument it is also configured to fly on the ER 2 research aircraft or on a research balloon package.

An engineering team has been formed under the direction of Roger Hedlund of the Ames Electronic Systems Branch. A prototype of the Argus instrument has been assembled. The prototype design relies on extensive optical system simulations carried out using an optical CAD system. It incorporates all the functions of the planned flight instrument and is currently being used to run extensive simulations of the instrument performance. The instrument employs a number of technical innovations and is pushing hard on the lower limits of size, weight, and power consumption, the latter considerations being critical to its efficient use in the Perseus aircraft research program.

A preliminary review of the Argus design, with scientific and engineering peers in attendance, was held at Ames in May of this year. Actions in the form of comments and criticisms from those attending the review are being considered by the engineering team.

Future milestones in the development of Argus include a critical design review in October of this year followed by instrument fabrication and lab testing of the finished instrument. We anticipate having Argus ready for flight testing in the third quarter of CY 1993.

Journal Publications

None

Development of Trace Gas Constituent Measurement Techniques for HSCT Engines and Their Components

Investigators

*R. C. Miake-Lye
J. Wormhoudt
K. Annen
C. Kolb
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821-3976

Research Objectives

Measurements of trace exhaust constituents are proposed in order to more completely characterize HSCT stratospheric emissions. This more detailed characterization is motivated by the need to quantify levels of species that would be active in heterogeneous chemistry in the plumes and wakes of these aircraft. Furthermore, accurate inputs to both the plume/wake modeling and the global atmospheric modeling require complete and accurate accounts of SO_x and NO_y being injected into the atmosphere. The program proposed involves collaboration with NASA to assess and prioritize exhaust gas composition measurements required for both existing aircraft gas turbine engines and prototype components of HSCT engines, followed by definition of an optimal measurement approach using either tunable diode laser absorption or tunable ultraviolet dye laser absorption. After the selection of the measurement technique and instrument development at ARI, a measurement program at HSR propulsion laboratories (including NASA LeRC and industry HSR labs) will follow, optimizing instrument performance at the measurement site, verifying sensitivity and detectability of the trace gas species, and providing emissions estimates of these for use in the NASA AESA atmospheric assessment program.

Summary of Progress and Results

A "strawman" list of trace exhaust species that needed to be measured was prepared at ARI based on ARI's wake modeling work, atmospheric laboratory chemistry studies, and discussions with global modelers. The list was developed around three categories: 1) species critical to global homogeneous and heterogeneous chemistry, 2) species relevant to global chemistry and/or involved in wake chemistry, and 3) species that do not need to be measured for either global or wake chemistry, but provide useful redundancy or calibration information. The NASA HSRP/AESA Engine Exhaust Trace Chemistry Committee met at Aerodyne on 21 April 1992 to review the strawman list of measurements and discuss measurement venues and measurement techniques. A draft report summarizing these conclusions was prepared and presented at the AESA Annual Meeting at Virginia Beach in May by R. Miake-Lye and also presented in a more expanded form at a workshop sponsored by NASA LeRC on 23-24 June.

Measurement techniques for the list of molecular species described above are being studied at Aerodyne. The focus has been on quantifying the capabilities of infrared and ultraviolet absorption spectroscopy, techniques which significantly increase the number of species that can be measured, while also allowing comparison with species measurements by other techniques. A key parameter in our feasibility estimates is the sample pressure, which varies through the range of in situ scenarios under consideration (flame tubes, combustor or combustor test rig, engine exit plane at sea level, and engine exit plane at simulated altitude), and also varies between those in situ diagnostics and the alternative option of coupling an absorption cell to existing extractive probes. Considerations in a tradeoff between in situ and extractive measurements include the latter's greater ease of comparison with conventional methods, its equal or greater sensitivity, and

the less stressful environment it offers the instrumentation. Balanced against these advantages is the fact that not all species will survive extractive sampling with their concentrations unchanged.

Journal Publications

None

Determination and Assessment of Emission Scenarios for the Program on Atmospheric Effects of Stratospheric Aircraft

Investigators

R. C. Miake-Lye
A. H. Epstein†
Charles E. Kolb
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821-3976

†A. H. Epstein is also associated with the
Department of Aeronautics and Astronautics
Massachusetts Institute of Technology
Cambridge, MA 02139

Research Objectives

Predictive modeling of the dispersal and reaction of stratospheric pollutants must be based on reliable projections of combustion emissions. An independent review and assessment of current efforts at NASA and industry combustor research centers will be directed toward supplying relevant projected emission data to the plume modeling effort. Current progress and future trends will be assessed for the control of critical exhaust species, as required by the concurrent modeling activity. A supplementary analysis stage will facilitate the integration of the emissions data into the modeling by identifying pollution chemical mechanisms to which the models may be particularly sensitive. Such integration will tie the required emissions scenario data to the needs of the plume modeling efforts and global stratospheric models.

Summary of Progress and Results

Emission estimates for NO, NO_2, CO, CO_2, H_2O, and SO_2 as well as particulates and unburned hydrocarbons were obtained from G. E. Aircraft Engines, Pratt & Whitney, and MTU Motorenund Turbinen Union of Germany based on their correlations developed using measurements of existing engines and their components, which were extended to HSCT operating conditions. These estimates were described in a report that was included as a chapter of the first HSRP/AESA annual report.

A workshop was held at Aerodyne on 13 March 1991 to bring together the engine development community, the atmospheric measurement community, and researchers interested in measuring engine exhaust constituents that are not currently measured in the existing diagnostic repertoire used in characterizing engine exhaust emissions. Presentations on the needs of the atmospheric community, existing measurement techniques, past and current measurement problems, and proposed new measurement techniques were made. Priorities of the AESA element of the HSRP were discussed in relation to possible measurement opportunities, from existing engines through HSCT engine components currently under development and on to fundamental laboratory experiments. The meeting participants recommended development of a program for measurements under AESA and for direction from the program concerning priorities both for what species must be measured and in which facilities relevant measurements can best be made.

Journal Publications

Miake-Lye, R. C., R. C. Brown, M. Martinez-Sanchez, and C. E. Kolb, Plume and wake dynamics, mixing and chemistry behind an HSCT aircraft, *J. Aircraft*, in press.

Laboratory Studies of Stratospheric Aerosol Chemistry

Investigators

Mario J. Molina
Department of Earth, Atmospheric and Planetary Sciences
and Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Research Objectives

The aim of the task is to generate and characterize in the laboratory aerosol particles similar to those formed in the high-latitude stratosphere, and to investigate the physical chemistry of the sulfuric acid-nitric acid-hydrogen chloride-water system in order to elucidate how polar stratospheric clouds are performed and their chemical reactivity associated with chlorine activation.

Summary of Progress and Results

Ice, nitric acid trihydrate (NAT), and sulfuric acid/water particles in the several micron size range simulating stratospheric aerosols have been generated using the diffusive trapping technique, and have been characterized using laser scattering techniques and FTIR spectroscopy.

Vapor pressures of H_2O, HNO_3, and HCl have been measured for the liquid $H_2SO_4/HNO_3/H_2O$ and $H_2SO_4/HCl/H_2O$ systems under conditions applicable to the polar stratosphere. The results indicate that the background aerosols consisting of liquid sulfuric acid solutions will absorb significant amounts of HNO_3 vapor under those conditions and that NAT crystals may form in the liquid droplets as precursors to type I polar stratospheric clouds. Also, the amount of HCl taken up by the liquid droplets in the polar stratosphere is small but sufficient to promote the heterogeneous reaction with $ClONO_2$ to produce Cl_2.

Journal Publications

Zhang, R., J. P. D. Abbatt, P. J. Wooldridge, and M. J. Molina, Vapor pressure measurements for the $H_2SO_4/HNO_3/H_2O$ and $H_2SO_4/HCl/H_2O$ liquid systems," *J. Phys. Chem.* (in preparation).

Molina, M. J., J. P. D. Abbatt, K. D. Beyer, J. Kim, P. J. Wooldridge, and R. Zhang, Physical chemistry of the $H_2SO_4/HNO_3/H_2O$ systems and formation of polar stratospheric clouds, *J. Geophys. Res.* (in preparation).

Real-Time Measurement of the Composition of Individual Aerosol Particles with a Mass Spectrometer

Investigators

*D. M. Murphy
A. F. Tuck
R/E/AL6
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303

Research Objectives

Chemistry involving aerosol particles is emerging as a crucial issue in stratospheric chemistry. Improved measurements of the composition of aerosol particles are needed. We are constructing an instrument that will make in situ measurements of the composition and size of individual aerosol particles. After passing through a differentially pumped nozzle to enter the instrument, aerosol particles then pass through the beam of a continuous laser. The scattered light both sizes the particles and provides a trigger for a pulsed laser that has sufficient intensity to produce ions when it strikes the aerosol particles. The ions will be analyzed with a time-of-flight mass spectrometer (TOF) to provide a complete mass spectrum for each aerosol particle.

Summary of Progress and Results

Accomplishments:

- Operating laser ionization time-of-flight mass spectrometer at the Aeronomy Lab:
  We have constructed all of the necessary experimental building blocks in our laboratory. We have successfully obtained mass spectra from a variety of test aerosols with excellent signal to noise.

- Logarithmic data collection:
  We have successfully constructed an effective ion detector for our application. It has two stages, each with a dynamic range of over 10^4. The gains overlap for an overall dynamic range in excess of 10^6. This dynamic range makes it possible to measure mass spectra from particles of widely varying size. Successfully measuring and digitizing ion currents over such a wide range at the 100 MHz bandwidth necessary for time-of-flight measurements is a significant achievement. The noise on this detector is more than satisfactory.

- Measurement of ionization thresholds at five wavelengths:
  We have measured the laser pulse energy necessary to produce ions from aerosol particles at 308 nm (XeCl) and 10.6 μm, with normal ionization followed by production of extremely energetic ions at slightly higher laser powers. This result has caused us to focus our efforts on an excimer rather than a CO_2 laser. (Trigger requirements eliminate YAG and most other lasers from consideration.)

- Development of two-stage aerosol inlet:
  We have developed a two-stage differentially pumped inlet in which the two nozzles are aligned to 0.001 in. without any adjustments. Such stable construction techniques are important for a future aircraft experiment.

- High-resolution spectrometer:
  We have designed a TOF that uses post-source post-focussing to bunch the ions and achieve higher resolution. So far, we have been able to achieve a resolution enhancement of approximately a factor of 3 over a simple linear TOF.

- Avalanche photodiode detector:
  We have installed a scattered light detector obtained from Particle Measuring Systems as the first step in our efforts to extend our system to particles as small as 0.4 μm in diameter.

In Progress:

- Smaller aerosol particles:
  We are obtaining equipment to generate well characterized test aerosols in submicron sizes, as well as continuing to improve the scattered light collection to be triggered by smaller particles. The mass spectrometer sensitivity is sufficient to analyze much smaller particles than we have to date (about 2 μm).
- Ambient particles:
  We plan to look at ambient particles in laboratory and outside air to test our system.
- Compact excimer laser:
  We have identified two designs of commercially available compact excimer lasers. At ~15 kg, they are comparable in size and power requirements to the diode-pumped YAG lasers proposed from some other aircraft experiments. We are working to purchase one of these lasers to evaluate its suitability for a future flight instrument.
- Mass spectrometer:
  We are working to further improve the performance of the mass spectrometer. Theoretical considerations indicate that another factor of 3 in resolution may be possible with little penalty in other parameters.
- Computer instrument control:
  We are continuing to computerize more aspects of the operation of the mass spectrometer, both for convenience and to gain experience for a future aircraft instrument.

Journal Publications

None

Transport Across Regions with Strong Isentropic Meridional Tracer Gradients: An Investigation Using Existing Lower Stratospheric Aircraft Measurements

Investigators

*Leonhard Pfister
Mail Stop 245-3
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035-1000

Henry B. Selkirk
Space Physics Research Institute
Sunnyvale, CA 94087

Research Objectives

Our work has two major objectives. The first is to examine the origin and nature of the thin (less than 1 km) layered structures in the tracer fields within the middle latitude lower stratosphere. In particular, we seek to establish the reversibility or irreversibility of these layers, whether they are produced by inertial gravity waves, and the nature and strength of the turbulence that erodes them. The ultimate goal is to show how important or unimportant they are to the overall meridional and vertical transport picture. The second objective is to extend the description of steep isentropic tracer gradients in the tropics as revealed by recent aircraft and satellite measurements by establishing the relationship to meteorological variables and potential vorticity.

Summary of Progress and Results

We have performed preliminary analysis of five science flights from the April 1986 Stratosphere-Troposphere Exchange Project middle latitude field program and completely analyzed one of these flights. Our findings so far:

- Layers as thin as a few hundred meters are horizontally coherent for distances of several degrees of latitude. Most appear to have little relationship to the wind field and are not caused by inertia-gravity waves.

- Inertia-gravity waves of significant amplitude are found in each of the five flights (peak-to-peak wind perturbations of up to 10 meters per second). They do not produce substantial tracer layering, however.

- Turbulence is more strongly related to the presence (more turbulence) or absence (less) of underlying topography than to the amplitude of inertia-gravity waves. However, in those regions where inertia-gravity waves are found, turbulence is found preferentially in the regions of strong, inertia-gravity-wave-induced shear.

Journal Publications

None

Black Carbon (Soot) Aerosols in the Lower Stratosphere: Abundance and Climatic Effects

Investigators

*Rudolf F. Pueschel
Kenneth G. Snetsinger
David F. Blake
Mail Stop 245-4
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035

Anthony D. A. Hansen
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

Research Objectives

Our objective is to (1) characterize existing black carbon (soot) aerosols (BCA) in the stratosphere and upper troposphere in terms of absolute amounts, sources, sinks, and residence times; (2) determine the single scatter albedo of the stratospheric aerosols and assess the effect of BCA on radiative transfer; and (3) assess the impact of BCA emissions from a prospective fleet of supersonic aircraft on BCA abundance and effects in the stratosphere.

Summary of Progress and Results

As determined by impactor samplers flown on ER-2 and DC-8 aircraft, BCA mass loadings in the stratosphere average 0.6 nanograms per standard cubic meter, or 0.01% of the total aerosol. Upper tropospheric BCA increases to 0.3%. Low stratospheric concentration is commensurate with present commercial air traffic fuel consumption, given the following assumptions: the BCA emissions are 0.1 grams per kilogram of fuel consumed, 10% of route mileage is above the tropopause, and average BCA stratospheric residence is about one year. Taking BCA into account, the stratospheric single scatter albedo is ≈ 0.99. Using parameters for planned supersonic commercial aircraft, whose emissions will be predominantly in the stratosphere, we show that such traffic will double stratospheric BCA concentration. This would reduce the aerosol single scattering albedo by 1%, and double the BCA surface area that is available for heterogeneous chemistry.

Journal Publications

Pueschel, R. F., D. F. Blake, K. G. Snetsinger, A. D. A. Hansen, S. Verma, and K. Kato, Black carbon (soot) aerosol in the lower stratosphere and upper troposphere, *Geophys. Res. Letts.*, in press.

Three-Dimensional Transport Studies with Assimilated Meteorological Data: Annual Cycles

Investigators

Richard B. Rood
Code 916
Atmospheric Chemistry and Dynamics Branch
Goddard Space Flight Center (GSFC)
National Aeronautics and Space Administration
Greenbelt, MD 20771

Research Objectives

This is a proposal to produce long-term meteorological data sets using data assimilation techniques. Winds from data assimilation models have been shown to provide the most realistic representations of stratospheric transport yet achieved. This proposal is to accelerate the production and improvement of long-term data sets so that transport of aircraft emissions in the lower stratosphere can be evaluated for the HSRP program. Having an in-house data assimilation system is essential for quantitative improvement of the transport characteristics of assimilated data products.

The original proposal called for production of a 20-month data set from the middle of 1987 through the winter of 1989. Citing programmatic requirements, HSRP asked instead for production of data sets that begin in September 1991, continuing through the HSRP-related aircraft expeditions in 1994. These data sets are expected to provide improved meteorological data during the Stratospheric Photochemistry Aerosols and Dynamics Expedition (SPADE) and SPADE-II. The assimilated data from this proposal are an essential part of the 3-D transport studies pursued by the HSRP proposal of Douglass et al. Newman et al. are expected to use the data from the SPADE mission in meteorological and trajectory studies. The data sets will be made available for the general scientific community.

Summary of Progress and Results

- The electronic link with the National Meteorological Center (NMC) has been shown to be adequate to provide the Data Assimilation Office (DAO) with level-2 data for near real-time assimilation. Personnel from the DAO and the Stratospheric General Circulation and Chemistry Project (SGCCP) have improved the internal transfer and preprocessing of the level-2 data. We are currently testing the system that produces near real-time analyses within 12-24 hours.

- Assimilated data sets have been produced for December 1991 and January 1992. These data sets are in zeroth-order quality evaluations. Intercomparisons to NMC analyses are under way and Upper Atmosphere Research Satellite (UARS) data are being used to provide critical independent checks. Level-2 data from September through the present have been archived and preprocessed, and will be assimilated as soon as wintertime transport experiments verify quality comparable to previous assimilation experiments.

- Working with personnel from the Douglass et al. HSRP proposal, we have improved the long-term transport characteristics of the assimilated data. Despite the previous successes with seasonal time-scale northern hemisphere winter simulations, long-term biases developed in the transport calculations. These were especially prominent in the tropics and subtropics. A post-processing technique has been developed that addresses this problem. Within the DAO, initialization techniques are being developed that also can address this problem.

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- The DAO has two assimilation systems that cover the lower stratosphere. Currently, tests are under way to evaluate whether the system with higher horizontal resolution (10 hPa top) or the system with lower horizontal resolution (0.01 hPa top) are more appropriate for HSRP needs. Experiments with enhanced vertical resolution in both the model and the analysis are under way.

- Transport experiments with the assimilated data sets have been used by Douglass et al. to compare 2-D and 3-D models. The assimilated data sets have also been used to evaluate tropical flight corridors and tropical middle latitude interactions. The assimilated data studies have revealed the importance of synoptic scale events in both lower stratospheric middle-latitude transport and chemistry as well as in stratosphere-troposphere exchange. Assimilation processes offer the best hope of obtaining realistic wind fields in the tropics.

- Access to other data sets: The DAO maintains an archive of ECMWF and NMC GDAS analyses for use by the GSFC community. These data sets have been used in transport calculations and in quality control of the DAO assimilation products.

Journal Publications

Rood, Richard B., Anne R. Douglass, and Clark J. Weaver, Tracer exchange between tropics and middle latitudes, *Geophys. Res. Letts.*, 19, 805-808, 1992.

Weaver, Clark J., Anne R. Douglass, and Richard B. Rood, Thermodynamic balance of three-dimensional stratospheric winds derived from a data assimilation procedure, submitted to *J. Atmos. Sci.*, 1992.

Heterogeneous Chemistry Relevant to the Effect on Ozone of Stratospheric Aircraft

Investigators

*K. R. Ryan
I. C. Plumb
R. D. Kenner
CSIRO Division of Applied Physics
P. O. Box 218
Lindfield NSW 2070
AUSTRALIA

Research Objectives

Our objective is to obtain quantitative information on rate parameters related to the mechanism of heterogeneous processes on polar stratospheric cloud particles. In particular, we wish to examine the reactions of NO_x and ClO_x species on water ice and nitric acid trihydrate surfaces over a range of temperatures and at concentrations comparable to those found in the stratosphere. To begin developing an experiment using fourier transform infrared (FTIR) to measure the detailed composition of the ice and nitric acid trihydrate (NAT) surfaces studied in the kinetic experiments and the nature of the changes taking place as the reactions proceed.

Summary of Progress and Results

The heterogeneous loss of several NO_x and ClO_x species on water ice and NAT surfaces have been studied using a flow reactor sampled by a mass spectrometer at temperatures in the range 160-205 K. The probabilities of loss of ClO, O_3, NO, NO_2, and Cl_2 from the gas phase upon collision with water ice and NAT at 183 K are all less than 10^{-4}.

A detailed study of the reaction of N_2O_5 with ice surfaces, in which a range of temperatures, carrier gas pressures, ice thicknesses, and N_2O_5 concentrations were examined, has been conducted. In all cases, the apparent reaction probability was found to decrease as a function of time and this decrease is attributed to poisoning of the ice surface by HNO_3. A model that corrected for the poisoning was developed to fit the data. Although the model was able to reproduce the data quite well for each experiment, the value of the reaction probability on pure ice calculated by the model depended on the experimental conditions. Several possible mechanisms, including pore diffusion, were investigated in an effort to understand the origin of the latter dependence. Experimental and modeling results suggest that reaction on the internal surface of the ice films prepared in this study is not a major loss mechanism for N_2O_5. The reaction probability of N_2O_5 on ice has a small negative temperature dependence over the temperature range 160-205 K.

The apparatus for studying surfaces using FTIR has been constructed and preliminary experiments are under way.

Journal Publications

Kenner, R. D., I. C. Plumb, and K. R. Ryan, Laboratory measurements of the loss of ClO on Pyrex, ice and NAT at 183 K, submitted to *Geophys. Res. Lett.*

Kenner, R. D., K. R. Ryan, and I. C. Plumb, A study of the reaction of N_2O_5 with ice surfaces over the temperature range 160-205 K, submitted to *J. Phys. Chem.*

Kenner, R. D., I. C. Plumb, and K. R. Ryan, Laboratory measurements of polar stratospheric cloud rate parameters, submitted to *1992 Quadrennial Ozone Symposium*.

Model and Measurements Data Base for Stratospheric Aircraft Assessments

Investigators

*Robert K. Seals, Jr.
Richard S. Eckman
Mary Ann H. Smith
Atmospheric Sciences Division
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665

Linda A. Hunt
Karen Sage
Lockheed Engineering and Sciences Co.
Hampton, VA 23665

Research Objectives

The purpose of this task is to support the use of model and measurement data sets to understand the response of the atmosphere to potential aircraft emission scenarios. The task focuses on compilation, distribution, intercomparison, and archival of such data sets in support of AESA studies and of associated workshops and intercomparison activities. Emphasis is on assembling relevant model prediction results and measurement data sets; making them available in an electronic format; and supporting the intercomparison, manipulation, and display of key parameters. The AESA work is complementary to activity under the Upper Atmosphere Data Program (UADP) funded through the NASA Upper Atmosphere Theory Program.

Summary of Progress and Results

The primary effort under this task has been working with the Models and Measurements Committee. Data were collected from 14 modeling groups, and several measured data sets were obtained and placed on the UADP standard grid for use in 15 intercomparison experiments. New measurement data sets included data from the SAGE II, TOMS, and SBUV satellite experiments; National Meteorological Center (NMC) temperature data and derived heating rates and circulations; and several recent balloon profiles. Support was provided both prior to and in real time at the February 1992 Models and Measurements Workshop. A new capability to generate and electronically transfer PostScript plot files provided high-quality graphics to researchers in remote sites; and the transportability of the workstation configuration enabled setup of the database system at the workshop location in Satellite Beach, Florida, for on-site support. Support was also provided for the HSRP/AESA annual meeting in May. Model projections based on the emission scenario data were received from seven modeling groups and added to the data base. Analysis and plots were done prior to the meeting and on-site support was provided.

Preparations are being made for the acquisition of high-speed civil transport (HSCT) emission scenarios from Boeing and Douglas. These data will be regridded and stored on the UADP system for distribution to the participating modeling groups. The data base will also serve as the repository for the resulting model projections to be used in preparing the 1993 assessment. Additional computer hardware and software were procured to streamline the data base and reduce costs. Interactive access will be moved from the UADP VAX to the Sun workstations by the end of FY 1992.

Journal Publications

None

Electron Microscope Aerosol Analysis for SPADE

Investigators

Patrick J. Sheridan
CIRES
Campus Box 449
University of Colorado
Boulder, CO 80309-0449

Research Objectives

There are two major objectives of this project, both of which require close cooperation with the University of Denver group. The first objective is to determine the collection efficiency of the new University of Denver electrostatic aerosol sampler (EAS) for particles of different sizes. The EAS has been designed to collect particles directly onto thin films, so that high-resolution analytical electron microscopy (AEM) can be used for aerosol analysis. The absolute collection efficiency of the new sampler for particles of different sizes is determined by comparing laboratory-generated, monodisperse particle loadings on the collection films with the input particle concentrations and flow rates. Thin-film aerosol loadings are characterized using AEM in either a manual or automated analysis mode. Aerosol samples collected on Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) test flights prior to deployment will also be inspected to insure reasonable particle loadings for AEM analysis.

The second goal of this project is to examine the physical and chemical properties of stratospheric particles collected with the EAS during the SPADE missions. The physicochemical characteristics of these particles and their stratospheric residence times will be of importance in determining the overall impact of HSCT emissions on stratospheric chemistry.

Summary of Progress and Results

The start date for the laboratory phase of this project was 1 April 1992. As of the end of July, approximately eight electron microscope sessions have been conducted to characterize and optimize the EAS collection efficiency for several size ranges of submicrometer particles. Observations from these sessions have resulted in design changes to the sampler which have significantly increased the EAS aerosol collection efficiency.

Journal Publications

Sheridan, P. J., R. C. Schnell, J. D. Kahl, J. F. Boatman, and D. M. Garvey, Microanalysis of the aerosol collected over south-central New Mexico during the ALIVE field experiment, May-December, 1989, *Atmos. Environ. 26A*, 1992, (in press).

Validating the Transport Component of Two-Dimensional Chemical Transport Models Using Excess Carbon 14 Data

Investigators

*Run-Lie Shia
Malcolm K. W. Ko
Rao V. Kotomarthi
Min Zou
Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, MA 02139

Research Objectives

An important factor in the assessment of atmospheric effects from the engine emissions of a projected fleet of stratospheric aircraft is the magnitude of the residence time of the emitted materials in the stratosphere. For species that have a photochemical lifetime longer than a year, the residence time depends on the cross tropopause exchange rate. Refinements are needed in current two-dimensional chemical transport models to provide better simulation of the exchange processes between the stratosphere and the troposphere. These refinements would include increasing the model resolution in the vertical to about 1 km and improving the model physics through validating the transport component of the model using excess ^{14}C data from nuclear bomb tests.

Summary of Progress and Results

We have completed an analysis in which various combinations of the transport parameters were used in a two-dimensional model, to see how well the excess ^{14}C from nuclear tests can be simulated. We found that the set of standard transport parameters used in the AER model produced very favorable results compared with the measurements. Only small adjustment (about 10%) could be justified.

The new version of the model with three times finer vertical resolution (Dz=1.2 km) has been used to investigate the cross tropopause transport. A detailed sensitivity study of excess ^{14}C simulation to the change of the transport parameters and tropopause height has been performed. The model simulations showed that, in the model, horizontal eddy diffusion along isentropic surfaces is the most important mechanism for transporting excess ^{14}C across the tropopause. Also we found that the model simulation is in better agreement with the measurements if the tropopause position shifts down one level (about 1.2 km) in the model. This shift of the tropopause would lead to a 5-7% increase in the accumulation of aircraft-emitted NO_x in the stratosphere.

Journal Publications:

None

Quantifying the Strength of Brewer-Dobson Circulation and Other Stratospheric-Tropospheric Exchange Processes

Investigators

*Ka Kit Tung
Department of Applied Mathematics, FS-20
University of Washington
Seattle, WA 98195

Research Objectives

The purpose of this research is to quantify the strength of the mass transport across the tropopause and to develop direct and indirect means to validate its strength, in support of the High Speed Research Program (HSRP) program of assessing the impact of stratospheric aircrafts.

Summary of Progress and Results

A direct method of deducing the strength of the Brewer-Dobson circulation is to perform radiative transfer calculations of the net heating rate in isentropic coordinates. Our result and its uncertainties are discussed in an article to appear in the Journal of Atmospheric Sciences.

A conference paper entitled "On the global exchange of mass between the lower stratosphere and troposphere" was presented at the HSRP/AESA Second Annual Meeting held on 17-22 May 1992 in Virginia Beach.

Participated in the Models and Measurements 92 Workshop and performed many 2-D model scenario runs.

Journal Publications

Olaguer, E., H. Yang, and K. K. Tung, On the radiative balance of the lower stratosphere, *J. Atmos. Science*, *49*, 15 July 1992.

C-3

Investigation of High-Altitude Aircraft Plumes and Contrails: Physical and Chemical Processes and Global Implications

Investigators

*Richard P. Turco
Department of Atmospheric Sciences
University of California
Los Angeles, CA 90024

Owen B. Toon
Earth System Sciences Division
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035

Research Objectives

We will develop a physical/chemical model describing the evolution and chemical effects of contrails formed behind high-speed stratospheric aircraft. The model will treat the formation and growth of ice particles and sulfate aerosols in an aircraft plume, and the chemical processing that occurs on these particles. Processes to be treated in detail include sulfuric acid and water vapor nucleation, condensational growth and evaporation of ice crystals, the behavior of soot aerosol in the presence of ambient sulfate particles, and the heterogeneous chemical processing of trace gases on particle surfaces. The model will be used to quantify important environmental effects of high-altitude flight including chemical transformations in the exhaust contrails (e.g., chlorine activation and de-NO_x-ification); impacts on the formation, distribution, and persistence of stratospheric sulfate aerosols and polar stratospheric clouds (PSCs); and perturbations of the chemical composition of the lower stratosphere caused by injected water vapor, nitric acid, and particulates.

Summary of Progress and Results

A physical/chemical model that describes the formation, evolution, and chemical effects of aerosol particles in the exhaust stream of high-speed stratospheric aircraft is currently operational. The contrail model predicts the formation and growth of ice and other particles in an expanding jet plume, and the heterogeneous chemical processes that may occur on the ice and other aerosols. The physics and chemistry leading to the formation of sulfate aerosols and polar stratospheric clouds are incorporated. Processes treated in detail include heteromolecular homogeneous and heterogeneous nucleation of sulfate aerosols, water vapor nucleation, condensational growth and evaporation as ice crystals, coagulation and sedimentation of the particle mixture, effects of the soot emissions, and heterogeneous chemical processing of trace gases on ice and other aerosol surfaces.

Nucleation Phenomena: We have developed a new, efficient algorithm for calculating the nucleation rates of sulfuric aerosols and ice crystals in aircraft wakes (Zhao and Turco, 1992) and in the perturbed stratosphere (Zhao et al., 1991, 1992). We used the model to study sulfuric acid nucleation on soot particles emitted by the aircraft engines. Both homogeneous bimolecular (H_2SO_4/H_2)) nucleation and heterogeneous binary nucleation on existing particles were considered. In particular, the nucleation rate was calculated for assumed emission factors of H_2SO_4 in the exhaust stream, on the grounds that a small fraction of the fuel sulfur would be oxidized by radicals into sulfuric acid. Similar algorithms were employed to compute the rates of sulfuric acid nucleation in the far wake environment, due to the delayed photochemical production of sulfuric acid vapor. Results were presented at High Speed Research Program

(HSRP) meetings in January 1991 and May 1992, and have been written up for publication (Zhao and Turco, 1992; also see Appendix A).

The basic studies of particle formation in aircraft wakes (Zhao and Turco, 1992) included comparisons of model predictions to limited wake observations of aerosol concentrations, size distributions, and composition, including insoluble cores. These comparisons confirmed the importance of sulfuric acid homogeneous nucleation of the contrail. Sensitivity tests to determine uncertainties in nucleation predictions for the conditions found in high-altitude aircraft contrails were also performed. Ice crystals are the most abundant particulates in aircraft contrails because of the high water vapor content of the exhaust. Our nucleation model computes homogeneous water nucleation rates and the nucleation rate of ice onto soot particles for a range of reasonable assumptions concerning soot properties (i.e., particle size distribution from test data and surface morphology from stratospheric soot samples analyzed at NASA Ames). Our calculations suggest that ice nucleation is highly dependent on environmental conditions and is most likely to occur on sulfate aerosols, which deliquesce into droplets that subsequently freeze.

The nucleation model was also used to investigate the conditions under which sulfate particle formation would be enhanced (Zhao et al., 1991, 1992). This study is relevant to the HSRP because sustained stratospheric flight will increase water vapor and sulfur concentrations, which in turn will enhance the probability of aerosol nucleation. Nucleation augments the total surface area of particles that are known to catalyze important chlorine and nitrogen heterogeneous reactions. Our analysis of this problem is continuing with specific applications to the HSRP.

Ice Microphysics: Our physical/chemical model stimulating the evolution and chemical effects of contrails formed behind high-speed stratospheric aircraft is now operational. In addition to the nucleation algorithms described above, the model includes water vapor condensational growth and evaporation for liquid droplets and ice crystals, the microphysical interactions of sulfate and soot particles through coagulation and ice scavenging, and the surface physics of trace gases on ice surfaces. We evaluated emission factor data and developed an empirical model for the temperature and mixing history of a high-altitude plume. These data were used to carry out preliminary simulations with the contrail microphysics model. By specifying the microphysical evolution of the particles in detail, we are providing realistic estimates for the surface areas available for chemical processing, and the duration of such processing in the wake. The microphysical contrail simulations also fill an important gap in the HSRP research and analysis plan.

The formation of long-lived contrails in the form of polar stratospheric clouds (PSCs) and possible heterogeneous chemical processing on these particles represent important uncertainties in the impacts of high-altitude aircraft on the stratosphere. Excess PSCs may form as a result of water vapor and nitric acid vapor accumulation in the lower stratosphere. Under the HSRP, we are investigating the persistence of contrails and the formation of excess aerosols under different stratospheric conditions, particularly those at high latitudes in winter and above the tropical tropopause (Drdla et al., 1992b). The simulations treat coupled contrail microphysics and chemistry, stimulate chlorine activation and nitrogen oxide reactions on ice particles (see following page), and predict the probability of PSC formation as a result of water vapor and NO_x emissions. These studies will be critical to a full photochemical assessment of the HSCT on stratospheric ozone.

Heterogeneous Chemistry: Models to describe the heterogeneous chemistry of ice particles in aircraft contrails were developed along two lines. For direct coupling to the microphysical model described above, the relationship between chemical reactions occurring on ice particles and the mass transfer rates between the gas phase and particle surfaces were defined in terms of "sticking coefficients," or reaction efficiencies, on ice derived from laboratory measurements (e.g., Drdla et al., 1991, 1992a,b). To achieve a more detailed understanding of possible variations in heterogeneous reaction rates, a basic microscopic phenomenological model for

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heterogeneous physical and chemical processes occurring on ice surfaces was also developed (Tabazadeh and Turco, 1991, 1992). The latter surface physics/chemistry model is based on fundamental concepts taken from surface physics. The model was applied to interpret and reconcile conflicting laboratory measurements of ice surface properties and chemical reactivities (Tabazadeh and Turco, 1992). The combined heterogeneous models provide a unique interface between laboratory investigations supported by the HSRP on the one hand and large-scale atmospheric photochemical models being used for HSRP impact assessments on the other.

Using the models just described, heterogeneous chemical processes occurring on ice particles in aircraft contrails are being studied at two scales -- as surface physics processes on individual particles and as macroscopic chemical effects of the particle ensemble. Trajectory calculations were carried out for aircraft exhaust air parcels subject to mixing and cooling. In addition, the model is being used to simulate the long-term evolution of perturbed air parcels with remnant exhaust characteristics. The microphysics and heterogeneous chemistry models were also attached to an existing gas-phase stratospheric photochemistry model to simulate the time-dependent compositional perturbations in the vicinity of an aircraft contrail. These coupled simulations allow us to assess the physical and chemical effects of high-altitude flight, offering more realistic predictions of input data for the larger-scale chemical models. The model is presently being applied to study the perturbation of the chemical composition of the lower stratosphere resulting from contrail formation, including effects of injected water vapor, soot particulates, and chemical transformations in the contrails (e.g., chlorine activation and de-NO_x-ification).

Other Contributions to the HSRP

R. Turco authored one of the baseline HSRP report chapters on the natural cycles and processes of stratospheric aerosols (Turco, 1992). Other research on stratospheric aerosols relevant to the HSRP was completed and published (Turco, 1991a,b; Turco and Hamill, 1992). Turco also chairs the Stratospheric Aerosol Science Committee (SASC) of the HSRP. SASC has deliberated on the experimental aspects of the HSRP related to aerosols and their effects. Two reports with specific recommendations have been prepared for HSRP program managers.

Project Personnel at UCLA (including part-time appointments)

Prof. Richard Turco (UCLA, Principal Investigator)
Prof. Patrick Hamill (San Jose State University, Consultant on nucleation and microphysics)
Dr. Sajal Kar (UCLA, Postdoctoral Researcher)
Katja Drdla (UCLA, Graduate Student)
Azadeh Tabazadeh (UCLA, Graduate Student)
Jingxia Zhao (UCLA, Graduate Student)

Journal Publications

Drdla, K., High-speed stratospheric aircraft: factors affecting their climatic effect, preprint 1991.

Drdla, K. and R. P. Turco, Denitrification through PSC formation: A 1-D model incorporating temperature oscillations, *J. Atmos. Chem., 12,* 319-366, 1991.

Drdla, K., R. P. Turco, J. Farrara, and C. R. Mechoso, PSC microphysics and heterogeneous chemistry along atmospheric trajectories, EOS Amer. Geophys. Union, Special Supplement, Fall 1991 AGU Meeting, p. 82, 1991.

Drdla, K., R. P. Turco, and S. Elliott, Heterogeneous chemistry on Antarctic PSCs: A microphysical estimate of the extent of chemical processing, *J. Geophys. Res.*, in press, 1992a.

Drdla, K., R. P. Turco, J. Bacmeister, M. R. Schoeberl, D. Baumgardner, and J. E. Dye, The efficiency of chemical processing in lee-wave polar stratospheric clouds, Trans. Am. Geophys. Union, EOS, Supplement, 1992 Spring Meeting, Montreal, p. 68, 1992b.

Elliot, S., R. P. Turco, O. B. Toon, and P. Hamill, Incorporation of stratospheric acids into water ice, *Geophys. Res. Lett., 17,* 425-428, 1990.

Elliot, S., R. P. Turco, O. B. Toon, and P. Hamill, Application of physical absorption thermodynamics to heterogeneous chemistry on polar stratospheric clouds, *J. Atmos. Chem.,* 1991.

Tabazadeh, A. and R. P. Turco, A surface chemistry model to study heterogeneous processes of atmospheric significance, EOS, Supplement, p. 82, October 29, 1991.

Tabazadeh, A. and R. P. Turco, A model for ice surface physics and chemistry, submitted to *J. Geophys. Res.*, 1992.

Turco, R., Volcanic aerosols: Chemistry, microphysics, evolution and effects, in Volcanism-Climate Interactions, L. S. Walter and S. de Silva (eds.), NASA CP-10062, Washington, DC, 1991a.

Turco, R., Middle atmosphere aerosols and their effects, *J. Geomag. Geoelect., 43,* in press, 1991b.

Turco, R., Upper-atmosphere aerosols: Properties and natural cycles, Chapter 3B, in The Atmospheric Effects of Stratospheric Aircraft: A First Program Report, M. J. Prather and H. L. Wesoky (eds.), NASA Ref. Publ. pp. 65-95, 1992.

Turco, R. P. and P. Hamill, Supercooled sulfuric acid droplets: Perturbed stratospheric chemistry in early winter, Ber. Bunsenges, *Phys. Chem., 96,* 323-334, 1992.

Zhao, J.-X. and R. P. Turco, Particle nucleation in the wake of a jet aircraft in stratospheric flight, to be submitted to *J. Geophys. Res.*, 1992.

Zhao, J.-X., O. B. Toon, and R. P. Turco, Simulation of condensation nuclei in the spring polar stratosphere, EOS Am. Geophys. Union, Special Supplement, Fall 1991 AGU Meeting, p. 82, 1991.

Zhao, J.-X., O. B. Toon, and R. P. Turco, Generation of condensation nuclei in the polar springtime stratosphere, submitted to *Geophys. Res. Lett.,* 1992

Aircraft Laser Infrared Absorption Spectrometer (ALIAS-II) for N_2O, CH_4, and H_2O Profiles from High-Altitude Unmanned Aircraft

Investigators

*Christopher R. Webster
Randy D. May
Jet Propulsion Laboratory
Mail Stop 183-401
California Institute of Technology
Pasadena, CA 91109

Kenneth K. Kelly
Adrian F. Tuck
R/E/AL6
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
Boulder, CO 80303-3328

Research Objectives

This task has two primary objectives:

- Upgrading, development, and participation of the ER-2 Aircraft Laser Infrared Absorption Spectrometer (ALIAS) for measurements of NO_2, HCl, N_2O, and HNO_3 for upcoming AESA/HSRP campaigns. Improved capability for diurnal studies of NO_2 and direct measurements of HNO_3 will enhance the existing ER-2 AESA/HSRP payload.

- Building of the new ALIAS-II for the Perseus aircraft. This powerful new miniature spectrometer will provide extensive measurements (high spatial resolution) of N_2O, CH_4, and H_2O as part of a reference chemical climatology data base for the lower stratosphere/upper troposphere. regions, investigating also the mechanisms responsible for stratosphere/troposphere exchange, and plume chemistry and physics with regard to dehydration processes in regions of particle formation.

Summary of Progress and Results

The ALIAS experiment for the ER-2 had a successful first campaign participation in the AASE-II missions of 19 October 91 - March 1992, demonstrating both the instrument concept and the measurement capability for HCl, N_2O, and CH_4. Since that time, extensive laboratory studies of high-frequency modulation methods have been interpreted to fully characterize their potential inclusion into the ALIAS instrument for a 6.2 µm wavelength channel for NO_2 measurement at the sub-50 pptv level. Interference fringe studies have revealed new insight into the laser absorption technique, and three new methods (harmonic addition, saw-cam spoiling, and multi-line summing) have been developed theoretically for experimental testing. The FM detector, vacuum station construction, and monochromator have all been procured as planned. In addition, ALIAS's gold mirrors have been recoated and installed for the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) campaign. Difficulties remain in obtaining suitable laser diodes for HNO_3.

ALIAS II is scheduled to be built beginning October 1992. The sampling configuration of utilizing a retroreflector located on the forward edge of the Perseus wing has been selected, with eventual upgrading to a multi-pass configuration for HCl or other gas measurements.

Journal Publications

Webster, C. R., R. D. May, C. A. Trimble, R. A. Chave, and J. Kendall, Aircraft Laser Infrared Absorption Spectrometer (ALIAS) for in-situ stratospheric measurements of HCl, N_2O, CH_4, NO_2, and HNO_3, submitted to *J. Geophys. Res.*, 1992.

Hodge, C. C. and C. R. Webster, High-sensitivity laser modulation techniques for aircraft and balloon-borne spectrometers: an experimental evaluation, submitted to *Applied Optics*, 1992.

Impact of Engine Emissions of a Proposed High-Speed Stratospheric Aircraft Fleet on the State of the Atmosphere

Investigators

*Malcolm K.W. Ko
Debra K. Weisenstein
Nien-Dak Sze
Jose M. Rodriguez
Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, MA 02139

Research Objectives

The AER 2-D chemistry-transport model will be used to investigate the sensitivity of ozone to emissions from high-speed civil transport (HSCT) aircraft, including nitrogen oxides, water vapor, carbon monoxide, hydrocarbons, and sulfur dioxide. Because heterogeneous chemistry was found to have a large impact on the predicted change in ozone due to HSCT emissions, a new emphasis is to develop a sulfate model in collaboration with Dr. Glenn Yue of NASA/Langley. AER will develop the gas-phase portion of the model which will be combined with the aerosol microphysics model at Langley. This model will allow us to predict changes in aerosol loading due to both aircraft and volcanic eruptions. The impact of changes in aerosol loading on ozone will be explored by varying the rate of the heterogeneous reactions over the expected range of the aerosol surface area.

Summary of Progress and Results

Model improvements in the past year have included updating the chemical rates to the JPL-90 recommendations, increasing the horizontal diffusion in the tropical lower stratosphere from 1×10^9 to 3×10^9 cm^2/sec, increasing the diurnal time resolution from 15 to 17 time points, and including heterogeneous chemical reactions on the background sulfate aerosol layer as recommended by the United Nations Environmental Program (UNEP). The changes in chemical rates resulted in smaller ozone changes due to the HSCT emissions. The change in horizontal diffusion resulted in somewhat greater impact in the southern hemisphere than previously predicted. The UNEP recommendation on aerosol surface area was about half of what we had used previously (Weisenstein, et al., 1991), and thus lessened the impact of heterogeneous chemistry on the ozone response to HSCT.

We repeated our model calculations with the seven HSCT emission scenarios that had been designated for intercomparison at the January 1991 Annual Meeting. The calculations were preformed with heterogeneous chemistry included, using background aerosol surface areas appropriate to nonvolcanic periods and with aerosol surface areas increased by a factor of four to simulate periods of volcanic activity. For the case of Mach 2.4 with NO$_x$ EI=15, the model predicts ozone column decreases of 1% or more at 60°N using background aerosols and no change at 60°N using enhanced aerosols. For the Mach 3.2 case with NO$_x$ EI=15, predicted ozone changes at 60°N are 3-4% depletion with background aerosols and 1-2% depletion with enhanced aerosols.

We have developed a gas-phase sulfur model which allows us to predict the change in stratospheric sulfate loading due to HSCT emissions. The model includes the species CS$_2$, DMS, H$_2$S, MSA, OCS, SO$_2$, and SO$_4$. Gravitational sedimentation velocities are used for SO$_4$ below 35 km. These values were calculated by Dr. Glenn Yue from the January-February 1989 SAGE II global aerosol distribution. The model calculates a stratospheric sulfate burden of 12.6×10^7 kg of sulfur without aircraft and 13.0×10^7 kg of sulfur with subsonic aircraft.

Assuming an EI of 1 for SO_2, the model predicts maximum local changes in sulfate due to HSCT emissions of 18%, 64%, and 94% for Mach 1.6, 2.4, and 3.2, respectively. Thus we expect changes of a factor of two or less in the aerosol surface area due to HSCT aircraft emissions with SO_2 EI=1. This is smaller than the factor of four aerosol range used for sensitivity tests of ozone impact and smaller than the range produced by volcanic eruptions.

Journal Publications

Weisenstein, D. K., M. K. W. Ko, J. M. Rodriguez, and N. D. Sze, Impact of heterogeneous chemistry on model-calculated ozone change due to high-speed civil transport aircraft, *Geophys. Res. Lett., 18*, 1991-1994, 1991.

Investigation of Combustion Aerosols as a Potential Sink for NO_x in the Expanding Exhaust Plume of the HSCT

Investigators

*Philip D. Whitefield
Donald E. Hagen
Cloud and Aerosol Science Laboratory (UMR/CASL)
Norwood Hall (G11)
University of Missouri-Rolla
Rolla, MO 65401

Harvey V. Lilenfeld
Mail Stop 111-1041
McDonnell Douglas Research Laboratories (MDRL)
McDonnell Douglas
P. O. Box 516
Saint Louis, MO 63166-0516

Research Objectives

Experiments are being performed to investigate the role of combustion aerosols as potential sinks for the NO_x in the exhaust plume of supersonic aircraft flying in the stratosphere. Laboratory-generated combustion aerosol (both fresh and aged) will be characterized for size distribution and hydration properties. Accommodation coefficients for NO and NO_2 will be measured for the aforementioned, well-defined combustion aerosols as a function of exposure time, relative humidity, pressure and temperature appropriate to conditions expected in the jet/vortex regime.

Summary of Progress and Results

Tasks 1 and 2 concerning the laboratory-generated combustion aerosol characterization are essentially complete. The following conclusions can be drawn from this work:

- Under LPP combustion conditions the jet fuels JP4, JP5, JETA, and JP8 produce sub-micron particulates with typical diameter range 0.014 - 0.2 microns, (b) typical distribution peak diameter range 0.03-0.05 microns and (c) typical critical supersaturations range 1.0 - 1.5 % for 0.035 micron diameter particulates.

- As stoichiometric conditions vary from lean to rich, typical size distributions broaden and shift to larger peak diameters.

- Critical supersaturation characteristics can be correlated to total sulfur impurity level in fuel.

Development work leading up to tasks 3 and 4 concerning the accommodation coefficient measurements have led to the following results:

- NO_x concentrations can be monitored in the cloud simulation chamber with critical orifice sampling to a quadrupole mass spectrometer.

- Monodisperse combustion aerosols have been generated in the simulation chamber at temperatures as low as 235 K and with diameters up to 5.00 microns.

Journal Publications

Hagen, D.E., M. B. Trueblood, and P. D. Whitefield, A field sampling of jet exhaust aerosols, submitted to *Particulate Science and Technology.*

Whitefield, P.D., M. B. Trueblood, and D. E. Hagen, Size and hydration characteristics of laboratory-simulated jet engine combustion aerosols, submitted to *Particulate Science and Technology.*

Abstracts of these papers can be found in the Proceedings of the 23rd Annual Meeting of the Fine Particle Society, 13-17 July 1992.

Detection and Analysis of Aircraft-Produced Particles in the Stratosphere: Instrument Development

Investigators

*James C. Wilson
Charles Brock
Department of Engineering
Knudson Hall
University of Denver
Denver, CO 80208-0177

Research Objectives

The research objective is to develop, integrate, and fly an instrument to measure the concentration of nonvolatile particles in the stratosphere and to collect particles for laboratory analysis. The nonvolatile particles are those surviving heating to 150°C. Sulfuric acid particles should vaporize at these temperatures and the remaining particles may be soot from aircraft engines. Aerosol samples will be collected to validate this assumption. A two-channel condensation nucleus counter is being built. One channel will count the particles sampled from the stratosphere and the second will count particles in a sample that has been heated to 150°C. A two-channel aerosol collector is also being built. One channel will collect particles larger than 0.1 micron in diameter by impaction. The second collector will use electric fields. The particles will be charged in a corona.

Summary of Progress and Results

This instrument is under construction for use in the SPADE mission of 1992. Test flights are scheduled for September 1992.

Journal Publications

None

High-Speed Research Program: Mission Scientist for SPADE

Investigators

Steven C. Wofsy
Department of Earth and Planetary Science
Harvard University
29 Oxford Street
Cambridge, MA 02138

Research Objectives

Planning for the first High Speed Research Program (HSRP) field mission, the Stratospheric Photochemistry, Aerosols, and Dynamics Experiment (SPADE), is in its final phases.

The HSRP is charged with assessing the potential impacts of stratospheric aviation on stratospheric chemistry and climate. The science questions and objectives relevant to SPADE can be summarized as follows:

1. What are the key chemical processes that potentially affect ozone levels in the part of the stratosphere most strongly influenced by stratospheric aviation?

   a. Free radical chemistry. SPADE is directed toward first-time measurements of HO_x radicals, in the context of a complete suite of chemical observations including NO, HNO_3, NO_y, ClO, BrO, O_3, HCl, and NO_2. A measurement of the light field will be included for the first time on an ER-2 chemistry mission, allowing more complete diagnosis of factors regulating concentrations of radicals than previously possible.

   b. Heterogeneous chemistry. Rates for key heterogeneous processes will be diagnosed by pseudo-diurnal measurements including darkness/sunrise, midday, and sunset/darkness. Particle and irradiance measurements are clearly important for this study.

The above are the priority #1 objectives.

2. What will be the distribution of exhaust effluents in the stratosphere?

The SPADE objective is to examine the distributions of a wide range of tracers in the lower stratosphere to provide essential tools for analysis of tracer transport in this region of the atmosphere.

Tracers selected to provide independent information cover a wide range of chemical lifetimes and for the first time include CO_2 as a non-reactive indicator of the age of the air and a tracer for input of tropospheric air into the stratosphere. A range of latitudes and altitudes will be surveyed.

Species: N_2O, CH_4, CFC's, CO, NO_y, CO_2, H_2O

Timing for SPADE and mission-critical criteria:

The fall was chosen to obtain relatively long nights to provide a clear signature for the heterogeneous processing of N_2O_5, avoiding winter conditions when parcels stripped from the polar vortex might be encountered.

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Diurnal studies are planned to observe diagnostic variations of radical species. This experimental design dictates operations from the NASA Ames Research Center in Moffett Field, California, to permit dark operations and minimize overhead on investigator time.

The two main science objectives (radical chemistry and tracer distributions in the lower stratosphere) were chosen to provide first order tests for key hypotheses, full flight tests and first field data for the HO_x, NO_2, CO_2, and uv-vis sensors, and to lay the groundwork for planning and execution of the HSRP field mission in 1994. Due to the large number and complexity of new instruments, planning has attempted to allow for potential schedule slips.

The investigations for SPADE are given below:

Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) Science Team
A Mission Sponsored by NASA's High-Speed Research Program
Moffett Field, CA
October 1992

Instruments:

Jim Anderson	Harvard University
Darrel Baumgardner	National Center for Atmospheric Research
Kris Boering	Harvard University
Roland Chan	NASA/Ames Research Center
Jim Dye	National Center for Atmospheric Research
Jim Elkins	NOAA/Environmental Research Laboratory
David Fahey	NOAA/Aeronomy Laboratory
Guy Ferry	NASA/Ames Research Center
Ken Kelly	NOAA/Aeronomy Laboratory
Max Loewenstein	NASA/Ames Research Center
Mike Proffitt	NOAA/Aeronomy Laboratory
Chris Webster	NASA/Jet Propulsion Laboratory
Paul Wennberg	Harvard University
Chuck Wilson	University of Denver

Modeling and Analysis:

Anne Douglass	NASA/Goddard Space Flight Center
Pat Hamill	San Jose State University
Jose Rodriguez	Atmospheric and Environmental Research, Inc.

Ancillary Measurements and Mission Support:

Steve Gaines	NASA/Ames Research Center
Paul Newman	NASA/Goddard Space Flight Center
Sam Oltmans	NOAA/Environmental Research Laboratory
Lenny Pfister	NASA/Ames Research Center
Ross Salawitch	Harvard University
Mark Schoeberl	NASA/Goddard Space Flight Center
Pat Sheridan	NOAA
Glenn Yue	NASA/Langley Research Center

International Guest Investigator:

      Guido Visconti   Universita' Degli Studi - Dell'Aquila

Project Office:

Steve Wofsy	Harvard University
Art Schmeltekopf	Retired, NOAA
Steve Hipskind	NASA/Ames Research Center
Michael Prather	University of California, Irvine
Richard Stolarski	NASA/Goddard Space Flight Center
Steve Wegener	NASA/Ames Research Center
Howard Wesoky	NASA/Headquarters
Kathy Wolfe	ARC Professional Services Group

Development of a High Sensitivity, Fast Response Instrument for In Situ Determination of CO_2

Investigators

*Steven Wofsy
Kristie A. Boering
Bruce C. Daube
Department of Earth and Planetary Science
Harvard University
29 Oxford Street
Cambridge, MA 02138

Darin Toohey
Department of Geosciences
216 Physical Sciences Research Facility
Unversity of California
Irvine, CA 92717

Ralph Keeling
Atmospheric Chemistry Division
National Center for Atmospheric Research
P. O. Box 3000
Boulder, CO 80307

Research Objectives

A fast response CO_2 sensor, with precision and accuracy better than 0.1 ppm in 10 secs, has been developed with HSRP support for the ER-2 aircraft. It will be flown in the SPADE mission (HSRP field experiment, Stratospheric Photochemistry, Aerosol and Dynamics Experiment) in California during Fall 1992. The measurements are intended to provide direct information on the age of stratospheric air to help characterize and validate/invalidate models being used to assess impacts of HSCTs on the atmosphere.

Journal Publications

None

Development of Lightweight NO_y Measurement System

Investigators

*Steven Wofsy
B. C. Daube
Department of Earth and Planetary Science
Harvard University
29 Oxford Street
Cambridge, MA 02138

David Fahey
J. W. Munger
J. D. Burley
R/E/AL6
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303-3328

Research Objectives

A lightweight NO/NO_y instrument is needed to explore the source and sink regions for stratospheric NO_x, especially tropical altitudes above 22 km. Recent progress in understanding NO_x has emerged from diverse instruments on the ER-2, which cannot reach these altitudes.

Summary of Progress and Results

A new, lightweight (49 kg) two-channel NO/NO_y instrument was constructed, where nitric oxide was detected by titrating with O_3 and detecting chemiluminescence of NO_2. Since the chemiluminescence of NO_2 is quenched at pressures > 1 mb, the detector is sensitive to the mole fraction of NO, and the sensitivity depends on volume flowrate rather than mass flow. A lightweight, high-performance lobe pump was used to move air at 2 liters through each channel at ambient pressure, and an ultralight ozonizer was developed capable of providing the large ozone flows required in this configuration.

The first test flights were conducted in Sonderstrom, Greenland (60N, 65W), in February and March 1992, in order to couple a possible scientific return with the ongoing polar mission, the Airborne Arctic Stratosphere Expedition (AASE-2). The payload consisted of the NO/NO_y instrument and J. G. Anderson's $ClO/O_3/P/T$ measurements with an integrated data system. It was recovered on the Greenland ice sheet.

Excellent results were obtained for NO, although data for NO_y was compromised by a contaminated component. In combination with the ClO observations, the data clearly show the effects of aerosols from Mt. Pinatubo, suppressing NO and enhancing ClO in the aerosol layer, with the reverse effect above the aerosol layer (likely due to changes in the uv-irradiance). The test flights indicate a smooth road to a fully operational NO/NO_y sensor.

Journal Publications

A publication is being prepared on these results.

Heterogeneous Chemistry Related to Stratospheric Aircraft Emissions

Investigators

*Douglas R. Worsnop
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821

Steven C. Wofsy
Department of Earth and Planetary Science
Harvard University
29 Oxford Street
Cambridge, MA 02138

Research Objectives

A laboratory program is investigating the heterogeneous chemistry of stratospheric aerosols, composed of mixtures of H_2SO_4, HNO_3, HCl, and H_2. The project has two tasks, (1) thermodynamics, i.e., measurements of aerosol vapor pressures and composition under simulated stratospheric conditions and (2) kinetics, i.e., measurements of the rates of uptake and reaction of gaseous species such as N_2O_5, NCl, HNO_3, and $ClONO_2$ on aerosol droplets.

Summary of Progress and Results

- The phase diagram of nitric acid hydrates has been remeasured and expanded. The thermodynamics of the dihydrate (HNO_3 *$2H_2O$) and a higher hydrate (possibly HNO_3 *$10H_2O$) have been determined. The dihydrate is only slightly less stable than the trihydrate (HNO_3 *$3H_2O$), the most stable phase under stratospheric conditions. Type I PSCs will most probably be composed of both HNO_3 *$2H_2O$ and HNO_3 *$3H_2O$. Lab observations indicate that metastable phases play a key role in nucleating nitric acid hydrates. In particular, initial formation of HNO_3 *$2H_2O$, followed by co-condensation of HNO_3 *$3H_2O$ and ice, provides a pathway for stratospheric denitrification by sedimentation of HNO_3-rich ice particles.

- HCl and N_2O_5 uptake rates into cold H_2SO_4/H_2 droplets (40-70 wt%, down to 230 K) have been determined. The mass accommodation coefficient of HCl is near unity at stratospheric temperatures, as predicted. HCl solubility in sulfuric acid is somewhat higher than previously reported, but still is relatively low. The low solubility and lack of surface adsorption ($<10^{-4}$ monolayers on lab droplets) serve to explain the low reactivity of HCl on liquid sulfuric acid compared to solid ice surfaces. N_2O_5 reactivity coefficients are consistent with other measurements (γ~0.1 at 230 K), showing weak negative temperature dependence and virtually no dependence on sulfuric acid composition.

Journal Publications

Worsnop, D. R., L. E. Fox, M. S. Zahniser, and S. C. Wofsy, Vapor pressures of solid hydrates of nitric acid: Implications for polar stratospheric clouds, submitted to *Science*.

Robinson, G. N., D. R. Worsnop, M. S. Zahniser, C. E. Kolb, and P. Davidovits, Uptake of HCl into sulfuric acid droplets as a function of composition and temperature, to be submitted to *J. Phys. Chem.*

2-D MAGI: Two-Dimensional Modeling of Aircraft Global Impacts

Investigators

*Donald J. Wuebbles
Douglas E. Kinnison
Keith E. Grant
Atmospheric and Geophysical Sciences Division, L-262
P. O. Box 808
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550

Research Objectives

This research project emphasizes the application of the LLNL 2-D chemical-radiative-transport model to determining the impact of present and potential future aircraft emissions on the global atmosphere. The intention is to reduce uncertainties and better define the range of possible effects of aircraft emissions on the atmosphere. Realistic scenarios for aircraft emissions are examined to evaluate past as well as future effects on the atmosphere. Further development and improvement of the model will be done to meet the special needs of the HSRP program. Tracer studies will contribute to the evaluation of the model's ability to treat lower stratospheric transport and tropospheric-stratospheric exchange processes. Radiative forcing effects on climate will be determined for aircraft scenarios.

Summary of Progress and Results

Our research studies during the past year have particularly focused on the effects of heterogeneous chemical reaction mechanisms in determining the potential impact on ozone from fleets of high-flying aircraft. These studies have been described in Kinnison and Wuebbles (1991, 1992) and in Ko et al. (1992a, b). Most of these analyses have centered on heterogeneous reactions involving sulfuric acid aerosols. Of particular importance is the reaction of N_2O_5 with water on these aerosols; however, we have also examined other reactions including a recent analysis of a new mechanism involving nitrosyl sulfuric acid (NSA). The net effect of the N_2O_5 reaction is a significant reduction in the effect on ozone from aircraft emissions of nitrogen oxides emitted into the stratosphere. The NSA chemistry has little additional effect on the ozone perturbation. It should be noted that many uncertainties still remain with respect to heterogeneous chemistry; we are currently investigating some of these uncertainties.

A number of improvements have been made to the LLNL two-dimensional chemical-radiative-transport model over the last year. The calculation of atmospheric dynamics has been revised to achieve a more self-consistent and interactive treatment of stratospheric processes. In addition to adding the heterogeneous processes, the chemical mechanism has been modified to fully treat temperature and pressure dependence of photolysis rates. A version of the code has also been developed with a much more comprehensive treatment of tropospheric chemistry.

We were extremely active in the planning and participation of the Models and Measurements Workshop. Doug Kinnison served on the planning committee, has led the discussion of the section on nuclear tracers, and has written a chapter for the report. Don Wuebbles was a participant in the preparation of several chapters. We also provided modeling results for every section of the Workshop.

Don Wuebbles is chairman of the Emissions Scenarios Committee. The committee met several times over the year. Reports of previous activities are described in Wuebbles et al. (1992) and Wuebbles (1992).

Journal Publications

Kinnison, D. E., Potential effects of aircraft emissions on ozone, Symposium of the Aspen Global Change Institute, also Lawrence Livermore National Laboratory report UCRL-JC-108398., 1991.

Kinnison, D. E. and D. J. Wuebbles, Future aircraft and potential effects on stratospheric ozone and climate, in Proceedings of the 42nd Congress of the International Aeronautical Federation, also Lawrence Livermore National Laboratory report UCRL-JC-108035., 1991.

Kinnison, D. E. and D. J. Wuebbles, Impact of supersonic and subsonic aircraft on ozone: Including heterogeneous chemical reaction mechanisms, in Proceedings of the Quadrennial Ozone Symposium, June 4-13, Charlottesville, VA, also Lawrence Livermore National Laboratory report UCRL-JC-108951, 1992.

Ko, M., D. Weisenstein, C. Jackman, A. Douglass, K. Brueske, D. Wuebbles, D. Kinnison, G. Brasseur, J. Pyle, A. Jones, R. Harwood, I. Isaksen, F. Stordal, and R. Seals, Ozone response to aircraft emissions: Sensitivity studies with two-dimensional models, Chapter 5 in *The Atmospheric Effects of Stratospheric Aircraft: A First Program Report.*, M. J. Prather, H. L. Wesoky, R. C. Miake-Lye, A. R. Douglass, R. P. Turco, D. J. Wuebbles, M. K. W. Ko, and A. L. Schmeltekopf, editors, NASA Reference Publication 1272, 1992a.

Ko, M. K. W., D. Kley, S. Wofsy, E. Zhadin, C. Johnson, M. Prather, D. Weisenstein, and D. J. Wuebbles, Predicted aircraft effects on stratospheric ozone, Chapter 9 in *Scientific Assessment of Ozone Depletion: 1991*, World Meteorological Organization report, in press, 1992b.

Prather, M. J., H. L. Wesoky, R. C. Miake-Lye, A. R. Douglass, R. P. Turco, D. J. Wuebbles, M. K. W. Ko, and A. L. Schmeltekopf, *The Atmospheric Effects of Stratospheric Aircraft: A First Program Report.*, NASA Reference Publication 1272, 1992.

Wuebbles, D. J., NASA High Speed Research Program Emissions Scenarios Committee report of meetings on September 26, 1991 and January 9, 1992. Lawrence Livermore National Laboratory report UCRL-ID-109860, 1992.

Wuebbles, D. J., S. L. Baughcum, J. H. Gerstle, J. Edmonds, D. E. Kinnison, N. Krull, M. Metwally, A. Mortlock, and M. Prather, Designing a methodology for future air travel scenarios, *The Atmospheric Effects of Stratospheric Aircraft: A First Program Report*, M. J. Prather, H. L. Wesoky, R. C. Miake-Lye, A. R. Douglass, R. P. Turco, D. J. Wuebbles, M. K. W. Ko, and A. L. Schmeltekopf, editors, NASA Reference Publication 1272, 1992.

Modeling of Microphysical Effects on Aerosol Properties Due to Stratospheric Aircraft Emissions

Investigators

*Glenn K. Yue
Lamont R. Poole
Mail Stop 475
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665-5225

Research Objectives

The objectives of this research are: (1) to better understand aerosol formation and growth mechanisms after expected increases in particles and trace gases caused by emissions from stratospheric aircraft and major volcanic eruptions, and (2) to assess the impact on optical properties of aerosol particles in the lower stratosphere and upper troposphere. The change of aerosol properties due to stratospheric aircraft and volcanic eruptions will be studied by analyzing the temporal and latitudinal variation of aerosol properties derived from the satellite experiment Stratospheric Aerosol and Gas Experiment (SAGE II).

Summary of Progress and Results

The Ruiz Cloud Experiment: The evolution of fine dust particles from the eruption of a volcano provides a unique tracer of stratospheric transport. The eruption of Ruiz in November 1985 was the strongest observed by SAGE II before the eruption of Mt. Pinatubo. The change of aerosol properties, including the optical depth and number concentration before and after the eruption of Ruiz, was studied by analysis of the SAGE II data set. Observations were compared with 2-D simulations. In the first few months of simulation, models do poorly. A few months later, there is reasonably good agreement between observations and model simulations when aerosol gradients have evolved and are smoother.

Optical Properties of Aerosol Particles after the Eruption of Mt. Pinatubo: In order to compare the impact of natural aerosol sources with that predicted from the HSCT and to estimate the depletion of ozone through heterogeneous chemistry after a major volcanic eruption, the change in the optical properties of aerosol particles after the eruption of Mt. Pinatubo was studied. The global mass loading of stratospheric aerosols due to Pinatubo is estimated to be about 30 megatons, which is much higher than the estimated 12 to 20 megatons due to El Chichon. The global distributions of the aerosol surface area for each month before and after the Pinatubo eruption are also estimated. These data are available for modelers to assess the impact of volcanic eruption on ozone depletion.

Aerosol Formation and Growth Mechanisms: The classical nucleation theory is applied to study the formation of new particles through homogeneous nucleation processes in the Pinatubo plume where high concentrations of SO_2 are present. The occurrences of high ratios of aerosol extinction at 0.525 micron to that at 1.02 micron at low altitudes observed by SAGE II are consistent with results of in situ measurements and the formation of ultrafine particles predicted by theory.

Comparisons of Remote Sensing and Correlative Measurements: In order to prepare for the SPADE mission and to validate the SAGE II data set after the eruption of Mt. Pinatubo, SAGE II measurements of aerosol and ozone are compared with results from lidar measurements. There

is general agreement in the altitude, intensity, and thickness of the volcanic layer observed by both systems.

Journal Publications

Yue, G. K., M. P. McCormick, and E. W. Chiou, Stratospheric aerosol optical depth observed by the Stratospheric Aerosol and Gas Experiment II: Decay of the El Chichon and Ruiz volcanic perturbations, *J. Geophys. Res., 96*, 5209-5219, 1991.

Yue, G. K., L. R. Poole, and M. P. McCormick, Mass loading of stratospheric aerosols after the eruptions of volcanos Ruiz, Kelut and Pinatubo, to be submitted to *Geophys. Res. Lett.*, 1992.

Yue, G. K., L. R. Poole, M. P. McCormick, and L. W. Thomason, Inference of stratospheric aerosol surface area from SAGE II measurements after the Pinatubo eruption, draft manuscript, 1992.

Appendix A

HSRP/AESA Program Report Chapter Reviewers

Appendix A
HSRP/AESA Program Report Chapter Reviewers

Dr. James G. Anderson
Atmospheric Research Project
Engineering Sciences Laboratory
Harvard University
40 Oxford Street
Cambridge, MA 02138

Dr. William H. Brune
Department of Meteorology
520 Walker Building
Pennsylvania State University
University Park, PA 16802

Mr. Willard J. Dodds
Mail Drop A-309
GE Aircraft Engines
1 Neumann Way
P. O. Box 156301
Cincinnati, OH 45215-6301

Dr. Anne R. Douglass
Code 916
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, MD 20771

Professor Frederick L. Dryer
Mechanical and Aerospace Engineering
D316 Engineering Quadrangle
Princeton University
Princeton, NJ 08544-5263

Professor Dieter H. Ehhalt
Institut fur Atmospharische Chemie, ICG-3
Forschungszentrum Julich
Postfach 1913
W-5170 Julich
GERMANY

Dr. William L. Grose
Mail Stop 401B
Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23681

Dr. David Hanson
R/E/AL2
Environmental Research Laboratory
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303

Professor James R. Holton
AK-40
Atmospheric Sciences
University of Washington
Seattle, WA 98195

Dr. Charles H. Jackman
Code 916
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, MD 20771

Professor Harold S. Johnston
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720

Dr. Douglas E. Kinnison
Atmospheric and Geophysical Sciences
  Division, L-262
Lawrence Livermore National Laboratory
7000 East Avenue
P. O. Box 808
Livermore, CA 94550-9900

Dr. Michael J. Kurylo
Code SEP
Headquarters
National Aeronautics and Space Administration
Washington, DC 20546

Dr. Ming-Taun Leu
Mail Stop 183-901
Jet Propulsion Laboratory
National Aeronautics and Space Administration
4800 Oak Grove Drive
Pasadena, CA 91109

Dr. Joel M. Levy
NOAA/Office of Oceanic and Atmospheric Research
OGP
1335 East-West Highway
Silver Spring, MD 20910

Dr. Nicole Louisnard
Physics Department
Office National d'Etudes et Recherches
  Aerospatiales
29 Avenue Division Leclerc
BP 72 92322 Chatillon Cedex
FRANCE

Dr. Jerry D. Mahlman
Geophysical Fluid Dynamics Laboratory
National Oceanic and Atmospheric Administration
Box 308
Princeton University
Princeton, NJ 08542

Professor Mario J. Molina
Atmospheric Chemistry, 54-1312
Department of Earth, Atmospheric, and
  Planetary Sciences
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. Michael Oppenheimer
Environmental Defense Fund
257 Park Avenue South, 16th Floor
New York, NY 10010

Professor R. Alan Plumb
Room 54-1726
Department of Earth, Atmospheric and
  Planetary Sciences
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. Michael J. Prather
Department of Geosciences
211 Physical Sciences Research Facility
University of California, Irvine
Irvine, CA 92717

Dr. A. R. Ravishankara
R/E/AL2
Environmental Research Laboratories
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303

Dr. Richard B. Rood
Code 910.3
Goddard Space Flight Center
National Aeronautics and Space Admin tration
Greenbelt, MD 20771

Dr. Arthur L. Schmeltekopf
410 East Fork Road
Marshall, NC 28753

Dr. Mark R. Schoeberl
Code 916
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, MD 20771

Dr. Richard S. Stolarski
Code 916
Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, MD 20771

Dr. Owen B. Toon
Space Sciences Division, Mail Stop 245-3
Ames Research Center
National Aeronautics and Space Administration
Moffett Field, CA 94035-4000

Mr. Felix J. Torres
Mail Stop AAC-1
Lewis Research Center
National Aeronautics and Space Administration
21000 Brookpark Road
Cleveland, OH 44135

Dr. Adrian Tuck
R/E/AL6
Aeronomy Laboratory
National Oceanic and Atmospheric Administration
325 Broadway
Boulder, CO 80303-3328

Dr. Robert T. Watson
Code SEU
Headquarters
National Aeronautics and Space Administration
Washington, DC 20546

Mr. Howard L. Wesoky
Code RJH
Headquarters
National Aeronautics and Space Administration
Washington, DC 20546

Dr. Steven C. Wofsy
Room 100A, Pierce Hall
Department of Earth and Planetary Science
Harvard University
29 Oxford Street
Cambridge, MA 02138

Dr. Donald J. Wuebbles
Atmospheric and Geophysical Sciences
  Division, L-262
Lawrence Livermore National Laboratory
7000 East Avenue
P. O. Box 808
Livermore, CA 94550

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Stolarski: Goddard Space Flight Center, Greenbelt, MD; Wesoky: NASA Office of
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16. Abstract This document presents a second report from the Atmospheric Effects of Stratospheric
Aircraft (AESA) component of NASA's High-Speed Research Program (HSRP). This
document presents a second report from the Atmospheric Effects of Stratospheric Aircraft
(AESA) component of NASA's High Speed Research Program (HSRP). Market and
technology considerations continue to provide an impetus for high-speed civil transport
research. A recent United Nations Environment Program scientific assessment has shown
that considerable uncertainty still exists about the possible impact of aircraft on the
atmosphere. The AESA has been designed to develop the body of scientific knowledge
necessary for the evaluation of the impact of stratospheric aircraft on the atmosphere. The
first Program report presented the basic objectives and plans for AESA. This second report
presents the status of the ongoing research as reported by the principal investigators at the
second annual AESA Program meeting in May 1992: Laboratory studies are probing the
mechanism responsible for many of the heterogeneous reactions that occur on stratospheric
particles. Understanding how the atmosphere redistributes aircraft exhaust is critical to our
knowing where the perturbed air will go and for how long it will remain in the
stratosphere. The assessment of fleet effects is dependent on the ability to develop
scenarios which correctly simulate fleet operations.

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